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COMPARISON OF METHODS FOR DETERMINATION OF NITROGEN DIOXIDE IN AMBIENT AIR

L. J. Purdue, et al

National Environmental Research Center
Research Triangle Park, North Carolina

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COMPARISON OF METHODS FOR DETERMINATION OF NITROGEN DIOXIDE IN AMBIENT AIR

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16. ABSTRACT

Four methods for the measurement of nitrogen dioxide in ambient air were studied concurrently to determine the intramethod and intermethod comparability of the data generated under a variety of carefully controlled conditions. Included were two automated continuous methods (chemiluminescence and colorimetric) and two manual methods (arsenite and TGS-ANSA). Simultaneous nitrogen dioxide measurements were made on a common air source using duplicate analyzers for each of the automated methods and quadruplicate samples for each of the manual methods. The study was conducted in three phases. Phase I measurements were made on ambient air to which extra NO_2 was added in order to provide a wider range of concentrations. Phase II was a limited study to determine the effect of variable NO_2 concentration fluctuations during a sampling period. Phase III was an investigation of suspected ozone interference with the automated continuous colorimetric method.

The results of the study indicate that the four methods, when properly used, are capable of producing data that are in remarkably good agreement except in the case of the colorimetric method, which yields low results in the presence of high ozone concentrations.

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COMPARISON OF METHODS FOR DETERMINATION OF NITROGEN DIOXIDE IN AMBIENT AIR

by

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Quality Assurance and Environmental Monitoring Laboratory

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CHEMICAL NAMES AND FORMULAS

Acetic acid	CH_3COOH
Ammonia	NH_3
8-Anilino-1-naphthalene sulfonic acid ammonium salt (ANSA)	$8\text{-}C_6H_5NH\text{-}1\text{-}C_{10}H_6SO_3\text{-}NH_4^+$
Carbon dioxide	CO_2
Carbon monoxide	CO
Formaldehyde	$HCHO$
Guaiacol (see o-methoxyphenol)	
Hydrochloric acid	HCl
Hydrogen peroxide	H_2O_2
Methanol	CH_3OH
o-Methoxyphenol	$CH_3O\text{-}C_6H_4\text{-}OH$
2-Naphthol-3,6-disulfonic acid disodium salt	$HO\text{-}C_{10}H_5(SO_3Na)_2$
N-(1-naphthyl)-ethylene diamine dihydrochloride (NEDA)	$[NH\text{-}C_{10}H_7(CH_2)_2NH_2]2HCl$
Nitric oxide	NO
Nitrous oxide	N_2O
Ozone	O_3
Phenol	C_6H_5OH
Phosphoric acid	H_3PO_4
Sodium arsenite	$NaAsO_2$
Sodium hydroxide	$NaOH$
Sodium metabisulfite	$Na_2S_2O_3$
Sodium nitrite	$NaNO_2$
Sulfanilimide	$[4\text{-}(H_2N)C_6H_4SO_2NH_2]$
Sulfanilic acid	$NH_2\text{-}C_6H_4\text{-}SO_3H$
Sulfur dioxide	SO_2
Tartaric acid	$(CHOH\text{-}CO_2H)_2$
Triethanolamine	$[N(CH_2CH_2OH)_3]$

ABBREVIATIONS

Peroxyacetyl nitrate	PAN
Total sulfur	TS
Total suspended particulates	TSP

ABSTRACT

A study of four methods for the measurement of nitrogen dioxide (NO_2) in ambient air to determine the intramethod and intermethod comparability of the procedures under a variety of carefully controlled conditions is presented. Two of the methods were automated continuous methods and two were manual methods (24 hour integrated). The two automated methods were chemiluminescence and colorimetric (Lyshkow modification of the Griess-Saltzman method) procedures. The two manual methods were the arsenite and triethanolamine, guaiacol, sodium metabisulfite, 8-amino-1-naphthalenesulfonic acid, ammonium salt (TGS-ANSA) method (recently developed).

The study was conducted in three phases. Simultaneous nitrogen dioxide concentration data were obtained from a common source using duplicate NO_2 analyzers for each of the automated methods and quadruplicate samples were collected for each of the manual methods. Phase I was a 22-day experiment in which additonal NO_2 was added to the ambient air sampled in order to provide a wide range of NO_2 concentrations. Phases II and III were limited experiments to determine the effect of variable NO_2 concentration fluctuations during a sampling period and to investigate suspected ozone interference with the automated colorimetric method.

The most important conclusion drawn from the study was that the four NO_2 methods, when used by skilled technicians under carefully controlled conditions, are capable of producing data that are in remarkably good agreement.

The effect of variable NO_2 concentration fluctuations during a sampling period on the results produced by the methods was minor. Suspected interference of ozone on the automated colorimetric method was verified.

SUMMARY

The most important conclusion that can be drawn from the results of this study is that the four methods for measuring the NO_2 content of the ambient atmosphere, when used by skilled technicians under carefully controlled conditions, are capable of producing data that are in remarkably good agreement.

The variability within a given method was least with the chemiluminescence method, followed by the arsenite, the TGS-ANSA, and the continuous colorimetric methods. In the worst case, the colorimetric method, there was a small bias of 7.5 micrograms of NO_2 per cubic meter ($\mu g\ NO_2/m^3$) of air (0.004 part per million) between the data from the two analyzers. This bias was less than 1 percent of the full-scale range of the analyzers.

Intermethod comparisons of data obtained when sampling ambient air showed that the average difference between any of the methods was never greater than 7.5 $\mu g\ NO_2/m^3$ (0.004 ppm). This maximum difference occurred between the arsenite and the TGS-ANSA methods. In all cases, variability of the differences among the four methods was only slightly higher than the variability within each method. The correlation coefficients for the intermethod comparisons were greater than 0.985 in all cases.

No intermethod differences could be related to the concentrations of nitric oxide (NO), carbon monoxide (CO), carbon dioxide (CO_2), ozone (O_3), total sulfur (TS), and total suspended particulate matter (TSP) in the ambient air sampled. This finding is significant because the procedure for the arsenite method (Appendix A-3) states that NO is a positive interferent. At NO concentrations as high as 302 $\mu g/m^3$ (0.246 ppm), no interference was detected.

The effect of fluctuations in the NO_2 concentration during a sampling period on the results produced by the four methods was relatively minor. The method differences in almost all cases were within the 95 percent confidence interval determined for the intermethod comparisons of Phase I of the study.

Suspected interference by O_3 on the automated colorimetric method was verified. Significant negative interference was found at NO_2 concentrations of 75 and 100 $\mu g/m^3$ in combination with O_3 concentrations of 353 and 667 $\mu g/m^3$. At an O_3 concentration of 100 $\mu g/m^3$, no interference was detected. The effect of high O_3 concentrations on the performance of the other methods tested was minor relative to its effect on the colorimetric method.

The performance of all methods was monitored closely throughout the study. For the automated continuous measurement methods, the performance of the chemiluminescence analyzers was better than that of the colorimetric analyzers in terms of zero drift, span drift, response times, and overall operation. Of the two methods,

the arsenite method is less susceptible to analytical variables such as reagent addition time or blank problems.

The good agreement between the ambient data generated by the continuous and manual methods validates the calibration procedures and is an indication that the methods tested are capable of producing accurate NO_2 data, with the exception of potential O_3 interference in the continuous colorimetric method.

COMPARISON OF METHODS FOR DETERMINATION OF NITROGEN DIOXIDE IN AMBIENT AIR

1. INTRODUCTION

On June 14, 1972, the Administrator of the Environmental Protection Agency (EPA) stated that the reference method for measurement of nitrogen dioxide (NO_2) concentrations in ambient air[1] was suspected of being unreliable[2]; results of laboratory testing and NO_2 measurements made over a period of several months at a large number of locations suggested apparent deficiencies associated with routine field use of the method. Accordingly, the Administrator announced that the reference method would be reevaluated.

The problems relating to the routine field use of the reference method for monitoring ambient concentrations of NO_2 were addressed in some detail in the Federal Register of June 8, 1973[3], in which the Administrator stated that it had not been possible to resolve the variable collection efficiency problem and that this method could no longer serve as the official reference method. Based on statements in the Federal Register of June 8, 1973, it was concluded that at least three other NO_2 measurement techniques were worthy of consideration as a replacement. Two of these were automated continuous measurement methods -- a chemiluminescence method (described in Appendix A-1) and a colorimetric method (described in Appendix A-2); the third was a manual, integrated (bubbler)method, using sodium arsenite (described in Appendix A-3). A fourth method, the TGS-ANSA (triethanolamine, guaiacol, sodium metabisulfite, 8-anilino-1-naphthalenesulfonic acid ammonium salt) method, was included in the study reported here on the basis of additional test data. The TGS-ANSA method was not listed in the Federal Register[3] because, at the date of that publication, it had not been sufficiently tested to determine whether it merited further consideration.

Because of the need for an adequate measurement method for ambient NO_2, an intensive study of these four methods was carried out by EPA to compare the results obtained by use of these methods under a variety of conditions.

OBJECTIVES

The basic objective of the study was to determine the intramethod and intermethod comparability of each of the four ambient NO_2 measurement techniques when sampling the same atmosphere under a variety of carefully controlled conditions. The study was conducted in three phases.

Phase I was designed to investigate intramethod and intermethod variability over NO_2 concentration ranges expected to occur in ambient air. Measurements of the ambient concentrations of nitric oxide (NO), carbon monoxide (CO), carbon dioxide (CO_2), ozone (O_3), total sulfur (TS), and total suspended particulate matter (TSP) were made concurrently during this phase of the study to provide data for use in determining whether any intra- or intermethod differences could be attributed to interference by any of these pollutants.

Phase II was a limited experiment designed to determine the effect, if any, of NO_2 concentration fluctuations during a sampling period on the comparability of the methods. To minimize the variability caused by other pollutants, this phase of the study was conducted by sampling clean air with controlled NO_2 additions, rather than by sampling ambient air.

Phase III was designed to investigate suspected interference of O_3 on the automated colorimetric method[4] and to determine the effect of O_3 on the other methods.

2. STUDY DESIGN

Because of the complexity of the study and the magnitude of effort required for its conduct, a detailed study plan was developed. To minimize variability resulting from operator errors and procedural variations, the study was conducted under the most favorable conditions. Meticulous attention was paid to the condition of equipment and the instructions to operating personnel regarding adherence to sampling procedures and quality control.

FACILITIES

All the instruments and equipment were located in the EPA Durham (North Carolina) Air Monitoring and Demonstration Facility (DAMDF), a building specially designed to permit the evaluation of air monitoring methodology. Ambient concentration data for NO_2 and other pollutants are routinely obtained at the DAMDF, which is equipped with a special glass manifold for the distribution of ambient air. The ambient air at this location was expected to contain at least moderate concentrations of NO_2 as well as many of the potentially interfering pollutants to the methods under comparison.

AIR DISTRIBUTION AND MONITORING SYSTEMS

A rather complicated physical system possessing considerable flexibility was required for this study. The basic air distribution system in the DAMDF was modified to permit the installation of the necessary instrumentation and the incorporation of the various subsystems used for the different phases of the study. The complete system, which is described in greater detail in Chapter 3 was comprised of the following subsystems: (1) the DAMDF air distribution system that supplied ambient air for the NO_2 methods under test and for the measurements of ambient pollutant concentrations; (2) a pollutant generation system for the addition of NO_2 and O_3 to clean air; and (3) a sampling manifold for the distribution of either ambient, clean, or spiked air to the intakes of the analyzers and samplers under test.

METHODS

Two of the methods tested are "automated methods" in which the sample collection and the analysis are performed by means of a continuous analyzer. One of the automated methods is based on the gas-phase chemiluminescent reaction between NO and O_3 at reduced or near-atmospheric pressure; NO_2 is measured as NO after quantitative conversion to NO. The other automated NO_2 method (continuous colorimetric) is based on a specific reaction of nitrite ion (NO_2^-) with diazotizing-coupling reagents to form a colored azo dye that is measured colorimetrically.

The other two methods are "manual colorimetric methods" in which the sample collection and analysis are performed separately. Samples are collected by passing air through

an absorbing solution at a constant flow rate for a prescribed time period. The samples are then transported from the field location to a central laboratory for analysis, which is based on a specific reaction of nitrite ion (NO_2^-) with diazotizing-coupling reagents to form a colored dye that is measured colorimetrically. Each method requires different absorbing solutions and diazotizing-coupling reagents.

Comparisons were made by simultaneously analyzing air from a common manifold for 22-hour periods using each of the methods. To determine the variability within a given method, data were collected by two identical continuous analyzers for each of the automated methods. Duplicate multiple gas bubbler samplers were employed for the collection of samples for the manual methods. Each sampler collected duplicate samples so that, for each sampling period, four concentration values were obtained for each of the manual methods and two values were obtained for each of the automated methods.

OPERATING SCHEDULE

All sampling periods were planned to be of approximately 22 hours duration (12 noon to 10 a.m.). The 2-hour period between 10 a.m. and 12 noon was needed for calibration of the continuous analyzers and for completion of other necessary tasks. All instruments used in a given phase were operated concurrently for the full sampling period. In the event of instrument breakdown or other problems, the day's operation was considered void for all methods and was repeated on the following day.

Phase I

Because of the relatively low atmospheric NO_2 concentrations encountered at the DAMDF, it was necessary to conduct this phase of the study by sampling ambient air to which NO_2 was added continuously to assure that the comparisons would be made over a wide concentration range. A 20-day sampling schedule was planned during which the NO_2-addition concentration was varied randomly from day to day. The following NO_2 addition concentrations were used: 0 $\mu g\ NO_2/m^3$ (0 ppm), 50 $\mu g\ NO_2/m^3$ (0.027 ppm), 100 $\mu g\ NO_2/m^3$ (0.053 ppm), 200 $\mu g\ NO_2/m^3$ (0.106 ppm), and 800 $\mu g\ NO_2/m^3$ (0.424 ppm). The schedule allowed for four daily periods of sampling at each of these NO_2-addition concentrations. Addition of 800 $\mu g\ NO_2/m^3$ was limited to 3 hours because concentrations at this level are not likely to occur for 22-hour periods.

In addition to the NO_2 measurements by the four methods under comparison, simultaneous analyses were made of the ambient air for NO_2, NO, O_3, TS, CO, and CO_2. High volume samples of TSP were collected outside near the ambient air intake of the DAMDF manifold during each period.

Phase II

The second phase of the study was conducted by sampling clean air to which known concentrations of NO_2 were added intermittently during the 22-hour sampling periods. The NO_2-addition concentrations were selected such that the resulting 22-hour-average concentration was either 100 $\mu g\ NO_2/m^3$ (0.053 ppm) or 200 $\mu g\ NO_2/m^3$ (0.106 ppm). The 8-day sampling schedule given below and shown graphically in Figure 1 was followed.

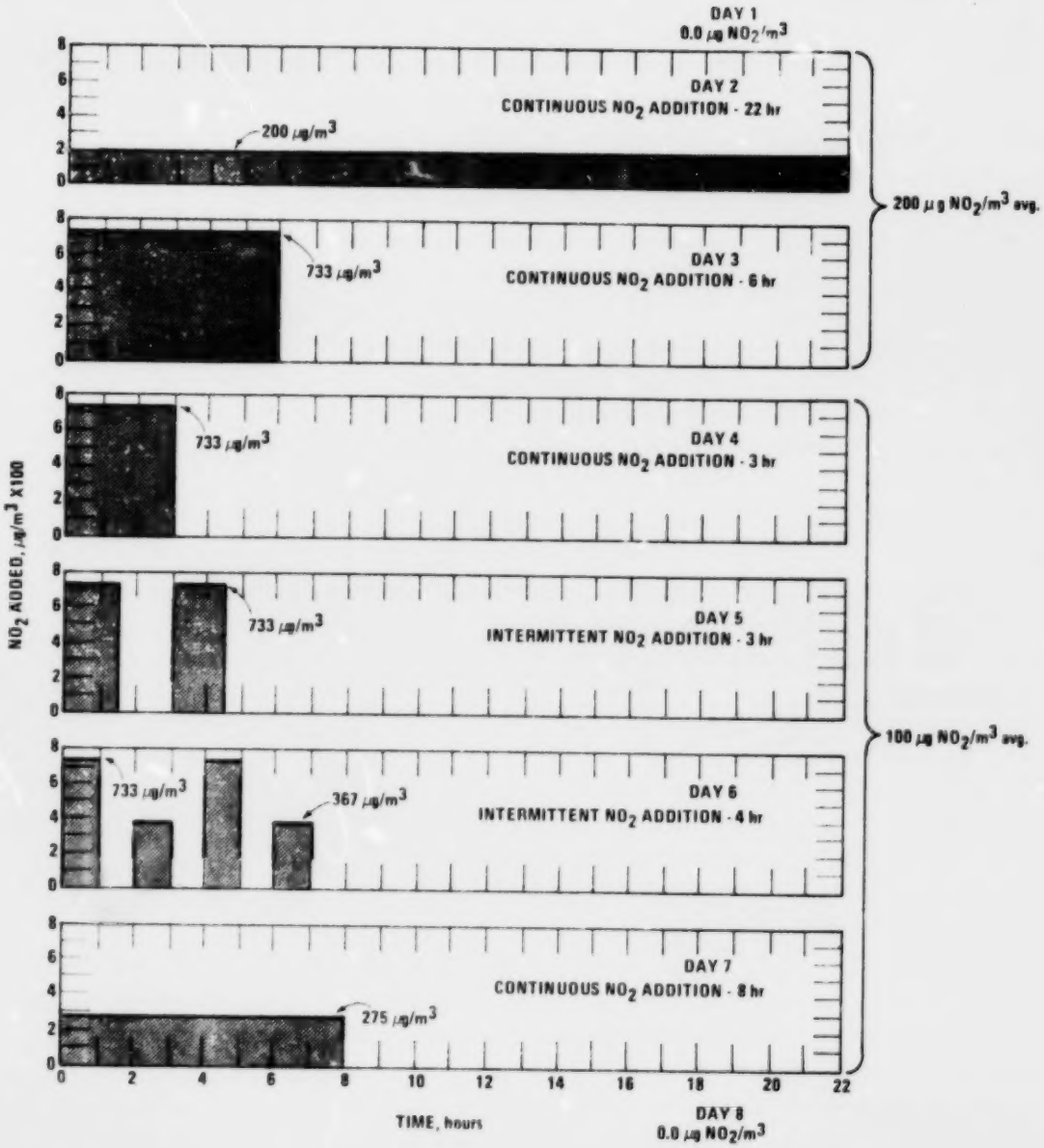

Figure 1. Phase II NO_2 addition schedule.

Day 1 (0 μg NO_2/m^3) - Clean, NO_2 free air.

Day 2 (200 μg NO_2/m^3) - Clean air spiked continuously at 200 μg NO_2/m^3.

Day 3 (200 μg NO_2/m^3) - Clean air spiked at 733 μg NO_2/m^3 for 6 hours and clean air for 16 hours;

Day 4 (100 μg NO_2/m^3) - Clean air spiked at 733 μg NO_2/m^3 for 3 hours and clean air for 19 hours.

Day 5 (100 μg NO_2/m^3) - Clean air spiked at 733 μg NO_2/m^3 for 1.5 hours and clean air for 2 hours; clean air spiked at 733 μg NO_2/m^3 for 1.5 hours; and clean air for 17 hours.

Day 6 (100 μg NO_2/m^3) - Clean air spiked at 733 μg NO_2/m^3 for 1 hour; clean air for 1 hour; clean air spiked at 366 μg NO_2/m^3 for 1 hour, clean air for 1 hour; clean air spiked at 733 μg NO_2/m^3 for 1 hour; clean air for 1 hour, clean air spiked at 366 μg NO_2/m^3 for 1 hour, and clean air for 15 hours.

Day 7 (100 μg NO_2/m^3) - Clean air spiked at 275 μg NO_2/m^3 for 8 hours, and clean air for 14 hours.

Day 8 (0 μg NO_2/m^3) - Clean, NO_2-free air.

Phase III

The possibility of O_3 interference was investigated by sampling known mixtures of NO_2 and O_3 in clean air. A 6-day sampling schedule (22-hour sampling periods) was planned to obtain data for each of the four methods using clean air containing the following mixtures of NO_2 and O_3:

Day	Nitrogen dioxide, μg/m³	Ozone, μg/m³
1	75	98
2	75	353
3	75	676
4	150	98
5	150	353
6	150	676

CALIBRATION

Initially, each of the chemiluminescence and colorimetric instruments was subjected to a 5-point calibration using the gas phase titration procedure described in the Federal Register of June 8, 1973[3]. Calibration of the manual bubbler methods was accomplished statically as described in the procedures (Appendices A-3 and A-4). Recalibrations were repeated as necessary.

DATA ACQUISITION

Responses of the automated analyzers to the NO_2 in the air sample were recorded on individual matched strip chart recorders. The strip chart traces were processed by the manual optical averaging procedure to obtain hourly average concentrations of NO_2 from which average concentrations for each 22-hour sampling period were computed. This

process is described in detail in Chapter 3. Concentration data from the manual bubbler methods were obtained by the process described in the procedures (Appendices A-3 and A-4).

3. EXPERIMENTAL

METHODS AND INSTRUMENTATION

The study was designed to simultaneously obtain NO_2 concentrations from a common source using duplicate analyzers for each of two automated NO_2 methods and collecting quadruplicate samples by each of two manual methods. Ambient concentrations of NO, CO, CO_2, O_3, TS, and TSP were also measured. Table 1 lists all the methods used for the study, an identification code for each, a designation as to whether the method is automated or manual, the operating range, and the sample flow requirements.

Comparison Measurements

Two model 8101-B chemiluminescence NO-NO_2-NO_x analyzers (Bendix Corporation) and two Air Monitor IV colorimetric analyzers (Technicon Instruments Corporation) were used to represent the automated NO_2 methods. The operational instructions and the calibration procedures for each of these methods are described in Appendices A-1 and A-2, respectively. Two gas bubbler samplers (Research Appliance Company), each capable of collecting five samples simultaneously, were utilized to collect two sets of duplicate samples by each of the manual methods.

Ambient Measurements

A third Bendix model 8101-B NO-NO_2-NO_x analyzer, a Bendix model 8002 chemiluminescence O_3 analyzer, a Bendix model 8301 flame photometric TS analyzer, a model LIRA 200 nondispersive infrared (NDIR) CO analyzer (Mine Safety Appliance Company), and a model 215AL NDIR CO_2 analyzer (Beckman Instruments, Inc.) were used to make ambient pollutant measurements. A standard high volume sampler (General Metal Works) was used to collect ambient TSP samples. The CO_2 analyzer was modified by mechanically offsetting the zero to 300 ppm CO_2 to provide a measurement range of 300 to 700 ppm. An integral strip chart recorder was used with each of the continuous analyzers to record the sensor response.

Table 1. POLLUTANT MEASUREMENT METHODS

Method	Analyzer	Automated	Manual	Range,[f] µg or ppm	Flow,[a] ml/min
Comparison Measurements					
Chemiluminescence (NO_2)	CM-1	X		0-0.5	139
Chemiluminescence (NO_2)	CM-2	X		0-0.5	137
Colorimetric (NO_2)	C-1	X		0-0.5	290
Colorimetric (NO_2)	C-2	X		0-0.5	290
	ARS-1		X	0.01-0.4	200
	ARS-2		X	0.01-0.4	200
Sodium arsenite (NO_2)	ARS-3		X	0.01-0.4	200
	ARS-4		X	0.01-0.4	200
	TGS-1		X	0.01-0.4	200
	TGS-2		X	0.01-0.4	200
TGS-ANSA[b] (NO_2)	TGS-3		X	0.01-0.4	200
	TGS-4		X	0.01-0.4	200
Chemiluminescence (O_3)[c]	O_3	X		0-0.5	1000
Ambient measurements					
Chemiluminescence ($NO+NO_2$)	CM-3	X		0-0.5	135
Chemiluminescence (O_3)	O_3	X		0-0.5	1000
Flame photometric (TS)[d]	TS	X		0-1.0	130
Nondispersive infrared (CO)	CO	X		0-50	2000
Nondispersive infrared (CO_2)	CO_2	X		300-750	2000
Hi-Vol sampler (TSP)	TSP		X	-	1.7[e]

[a] Sample flow rate in milliliters per minute.

[b] TGS-ANSA - Triethanolamine, guaiacol, sodium metabisulfite, 8-anilino-1-naphthalene sulfonic acid ammonium salt.

[c] This analyzer was used to monitor O_3 in the NO_2 sampling manifold during Phase III.

[d] Total Sulfur (TS) calibrated as Sulfur dioxide.

[e] Cubic meters per minute.

[f] Range in µg or ppm.

SAMPLING SYSTEM

The general sampling system schematic is shown in Figure 2. The manifold system was arranged so that ambient air could be drawn from the DAMDF ambient air manifold into a specially constructed NO_2- sampling manifold for sampling by the four methods under comparison. The DAMDF manifold is a multi-sampling port, all-glass system through which an excess of ambient air is drawn at a rate of approximately 10 liters per minute (liter/min). The intake of this manifold is an inverted glass funnel located 1.2 meters above the roof of the building (6 meters from ground level). The special NO_2- sampling manifold for the four methods under test was constructed from 2.5-centimeter (cm) internal diameter (I.D.) glass tubing and was designed to allow the uniform addition of known concentrations of gaseous pollutants to a clean or ambient air stream prior to introduction into the sampling manifold.

Ambient air was drawn through the NO_2-sampling manifold using a vacuum pump with a flow control valve and vacuum regulator that allowed the ambient air flow to be varied from 0 to 20 liters/min. A mass flow meter placed downstream from the sample ports provided an accurate measurement of this flow. The total flow through the system was the flow rate determined by the mass flowmeter plus the total air flow required for each of the test methods. The sample flow requirements for each of the analyzers and each of the bubbler samplers is given in Table 1. Air from each of the manifold sampling ports was analyzed for NO_2 to assure that the clean or ambient air and the added NO_2 were uniformally mixed and distributed throughout the NO_2-sampling manifold.

As shown in Figure 2, the sample intakes of the two chemiluminescence NO_2 analyzers were connected to a single 500-milliliter (ml) mixing flask, which was connected to the NO_2-sampling manifold. This mixing flask was used to minimize the occurrence of negative NO_2 responses caused by rapid changes of NO and NO_2 concentrations in the ambient air and to compensate for response time differences between the chemiluminescence and the colorimetric analyzers. The O_3 analyzer shown connected to the NO_2 sampling manifold was used only during Phase III.

Pollutant Generation

The pollutant generation system shown in Figure 2 was used for the addition of NO_2 and O_3 (Phase III) to the ambient air or the clean air in the NO_2-sampling manifold. Gravimetrically calibrated permeation tubes were used for generating NO_2 in a system similar to that described by Scaringelli, O'Keefe, Rosenberg, and Bell[5]. Nitrogen dioxide is introduced at a constant rate (100 cm^3/min) into the air stream, which is passed through the mixing chamber and then through the sampling manifold. The NO_2 concentration in the sampling manifold is the sum of the amount added and the amount present in the ambient air. The amount added was varied to

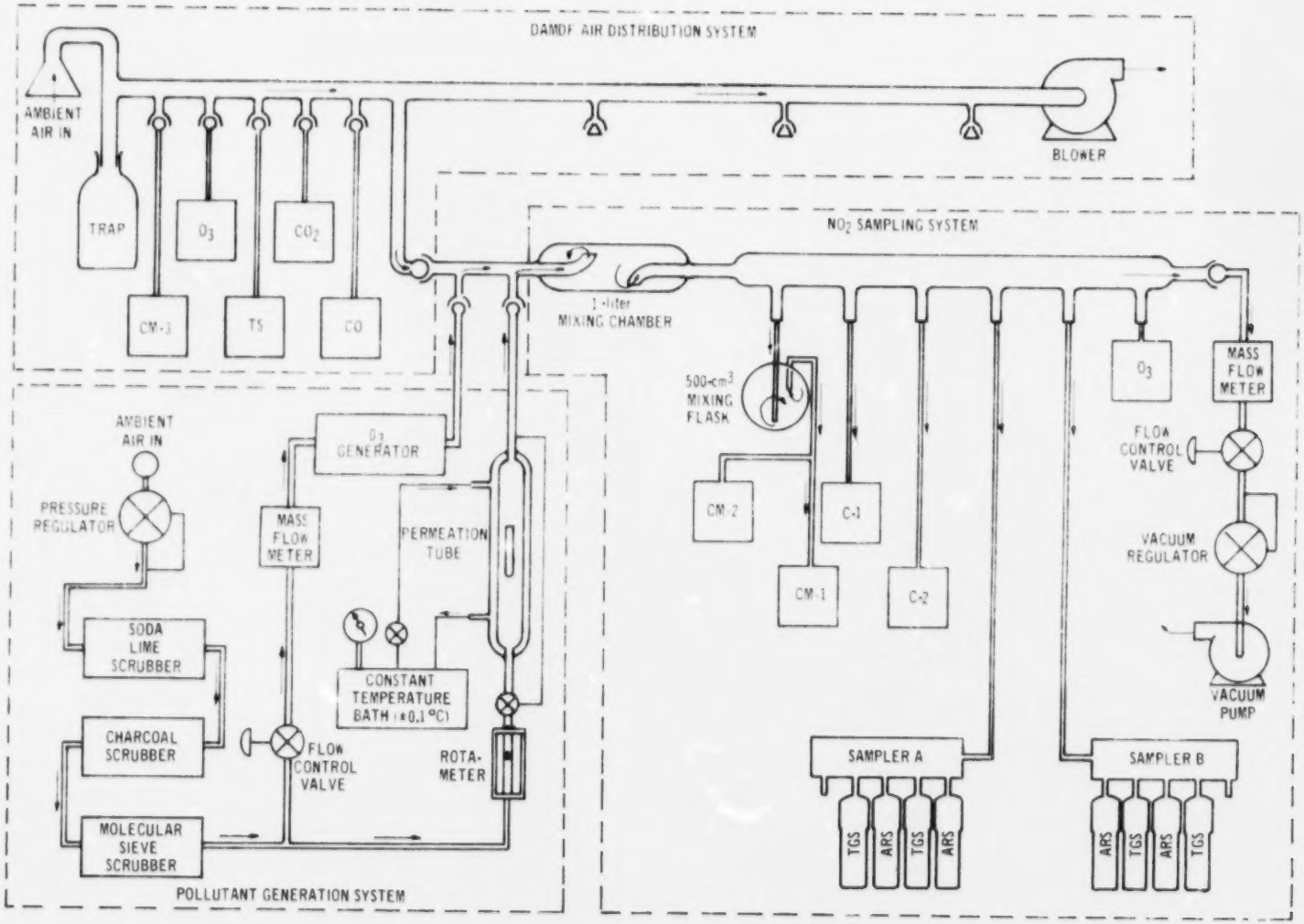

Figure 2. Sampling system. (See Table 1 for identification codes.)

obtain different NO_2 levels for each sampling period by either changing the total ambient air flow rate through the sample manifold, the number of permeation tubes in the chamber, or both. Permeation tubes with rates ranging from 1 to 2 μg NO_2/min were used in combination with ambient air dilution rates from 5 to 20 liters/min to allow the addition of NO_2 at concentration levels ranging from 0 to 800 μg/m^3. The flow rate through the NO_2-sampling manifold was never lower than 5 liters/min to assure that an excess of air was always available for all the methods under test, which required a total of approximately 2.5 liters/min.

Ozone was generated by passing clean air through an ultra-violet irradiated quartz tube into the NO_2-sampling manifold. The concentration of O_3 in the sampling manifold was varied by increasing or decreasing the surface area of the quartz tube exposed to the ultra-violet source.

TEST ATMOSPHERES

In Phase I, the NO_2-sampling manifold was connected to the DAMDF ambient air manifold as shown in Figure 2. The NO_2 was added to the ambient air stream from the DAMDF manifold in accordance with the planned random sampling schedule at the four NO_2 addition concentrations. Simultaneous ambient air measurements were made from the DAMDF manifold.

In Phase II, the NO_2 sampling manifold was disconnected from the DAMDF ambient air manifold, and clean dilution air was introduced into the NO_2-sampling manifold through the O_3 generator with the ultra-violet source turned off. The NO_2 was added intermittently to this clean air stream in strict accordance with the planned sampling schedule (Figure 1).

Phase III was conducted using the same sampling system used in Phase II. The NO_2 was added continuously to the clean air stream. Ozone was added continuously to this air stream by turning on the O_3 generator and adjusting the ultra-violet exposure of the air stream to obtain the desired O_3 concentrations. The O_3 concentrations in the sampling manifold were determined by the chemiluminescence O_3 analyzer shown in Figure 2.

START UP AND CALIBRATION

The chemiluminescence NO-NO_2 analyzers and the automatic colorimetric NO_2 analyzers were thoroughly examined by representatives of the respective analyzer manufacturers to assure that the instruments were operating properly and in conformance with the recommended procedures prior to initiation of the study. The chemiluminescence analyzers were operated on the 0 to 0.5 ppm (0 to 940 μg NO_2/m^3) full-scale range, which is the most sensitive and normally recommended operating range for ambient measurements. The operating range of the colorimetric analyzers was adjusted from the manufacturer's recommended operating range of 0 to 1.15 ppm to 0 to 0.5 ppm by a simple span control adjustment. This adjustment was made on the output of the colorimeter and did not affect the performance characteristics of the analyzers.

Initially, each continuous analyzer was set up and started in strict accordance with the manufacturer's operating instructions. Each analyzer's zero control was adjusted, using zero air, to obtain a + 5 percent offset on the recorder chart in order to facilitate observing negative drift. Each analyzer's span control was adjusted using dynamic standards to obtain a full-scale response equivalent to the range given for each analyzer in Table 1. A 5-point calibration curve was constructed to verify linearity for each of the analyzers. The chemiluminescence NO_2 analyzers and the colorimetric analyzers were calibrated using dynamic NO_2 standards prepared by the gas-phase titration technique.[3] A high pressure steel cylinder containing approximately 100 ppm of NO in nitrogen was used as the standard. This cylinder was assayed by gas-phase titration with known concentrations of O_3 from an O_3 generator calibrated with the neutral buffered potassium iodide (KI) procedure.[3] A Bendix Model 8851 calibration system was used to perform the gas-phase titrations. Following the initial calibration of each of the chemiluminescence and colorimetric NO_2 analyzers, the instruments were zeroed and spanned daily throughout the experiment. The continuous ambient O_3, TS, CO_2, and CO analyzers were zeroed daily and spanned at the beginning and end of the study.

The colorimetric analyzers were also statically calibrated using sodium nitrite standard solutions in water as recommended by the manufacturer. This calibration is based on the empirical observation that 0.72 mole of sodium nitrite produces the same color as 1 mole of NO_2. The static calibration produced a calibration curve with a slope that was 94 percent of the slope of the calibration curve obtained by using the gas-phase titration technique. Dynamic gas-phase titration calibration was used for this study to be consistent with the procedure followed for the chemiluminescence analyzers.

The manual methods were calibrated statically using sodium nitrite standards made up in the respective absorbing solutions for each method. Dynamic calibration of the manual methods was not required because the NO_2 collection efficiencies for each method has been predetermined,[6-8] and appropriate correction factors are included in the procedures.

The flame photometric TS analyzer was calibrated with a gravimetrically calibrated sulfur dioxide (SO_2) permeation tube. The NDIR CO and CO_2 analyzers were calibrated using standard calibration gases in high pressure cylinders. The O_3 analyzers were calibrated using an O_3 generator calibrated by the neutral buffered KI procedure.[3]

SAMPLING AND ANALYSIS PROCEDURES

The four methods were compared for 22-hour periods consistent with the recommended sampling period for the manual methods. Daily samples were collected for each of the manual methods for approximately 22 hours between 12:00 noon and 10:00 a.m. the following day. The automated methods, including the ambient analyzers, were operated concurrent with this period. During the 2 hours from

10:00 a.m. to 12:00 the automated NO_2 analyzers were zeroed and spanned and readjusted to the conditions of the initial calibration, if necessary; the NO_2 addition concentration was changed for the next day's experiment; and the eight absorption bubblers for the manual method were changed.

Prior to beginning each sampling period, the continuous NO_2 analyzer's sample inlet lines were connected to the calibration system containing clean zero air. The zero response for each analyzer was adjusted to 5 percent of chart, and the zero adjustment settings were recorded. A known NO_2 concentration between 60 and 90 percent of full scale (0.3 to 0.45 ppm) was generated using the gas-phase titration technique. After allowing the analyzers to reach a stable reading, the span control for each analyzer was adjusted to obtain a response equal to the response at the initial calibration. The appropriate permeation tubes were placed in the permeation tube chamber, and the air flow through the sampling manifold was adjusted to obtain the desired NO_2 addition concentration for the day's experiment. During Phase I of the study, the NO_2 was added to the ambient air stream. During Phases II and III, the NO_2 was added to a clean air stream. All sample inlet lines of the NO_2 analyzer were then transferred from the calibration system to the sampling manifold.

Two absorption tubes for each of the manual methods were placed in each of the two gas samplers, and the initial flow measurements for each of the bubbler trains were made and recorded. The absorption tubes for each method were positioned alternately in the gas samplers as shown in Figure 2. These positions were reversed daily to eliminate the possibility of manifold effects within the gas samplers.

A clean, preweighed, 8- x 10- inch glass fiber filter was placed on the high volume sampler. When the colorimetric analyzers stabilized at the new NO_2 concentration, the sampling period was initiated by the start of the gas samplers and the high volume sampler. An initial air flow measurement for the high volume sampler was taken immediately after the start of the sampling period.

At the end of the sampling period, the final flow measurements for each bubbler train and the high volume sampler were made, the samplers were shut off, and the time was recorded. The absorbing tubes were removed from the gas sampler and stored for subsequent analysis. The unadjusted zero and span control settings for each analyzer were recorded and compared with the settings at the beginning of the sampling period to verify that they were not changed during the sampling period.

All analyzer inlet lines were transferred from the NO_2-sampling manifold to the calibration system. An unadjusted zero was recorded for each analyzer and then readjusted, if necessary, to 5 percent of chart. An NO_2 concentration between 60 percent and 90 percent of full scale was generated, and after allowing the analyzers to reach a stable reading, the unadjusted span readings were recorded. The span controls for each analyzer were then adjusted, if necessary,

to obtain a response equal to the response at the initial calibration. The new zero and span control settings were recorded. All NO_2 analyzer inlet lines were transferred from the calibration system to the NO_2-sampling manifold, containing the NO_2 addition concentration for the next test day. The absorbing tubes for the next sampling period were placed in the gas samplers, the appropriate flow measurements were made, and the next sampling period was initiated.

Figure 3 is an example of a typical strip chart from a day's experiment for a chemiluminescence NO_2 analyzer. Between 10:00 a.m. and 12:00 noon before the start of the Day 2 test, the analyzer was zeroed and a known concentration of NO_2 was measured by the analyzer (unadjusted span); the analyzer response was then adjusted to the initial calibration response (adjusted span). The analyzer sample inlet was then put back on the NO_2-sampling manifold. At 12:00 noon the experiment was initiated by the start of the gas samplers (manual methods). At 10:00 a.m. the following day, the gas samplers were stopped, and the analyzers were zeroed (unadjusted zero) and readjusted if necessary (adjusted zero). An unadjusted span was taken and readjustment was made, if necessary, and preparations for the next day's experiment were made.

Strip chart values from the automated methods were converted to hourly averages for each day's experiment and recorded on data forms for submission for statistical analysis. Only hourly averages for time periods concurrent to the manual methods sampling periods were submitted for analysis. A base line for zero corrections was made by drawing a straight line between the adjusted zero at the beginning of each day's experiment and the unadjusted zero at the end of the day's experiment. The average reading in chart divisions for each hour was determined visually by drawing a straight line parallel to the chart division lines such that the area bounded by the trace and the two hour lines was equal on both sides of the line. This is illustrated in Figure 3 by hours 1200-1300 and 1400-1500. The baseline reading in chart divisions is subtracted from the hourly average reading, and this reading is converted to NO_2 concentration in ppm by reference to the calibration curve. Concentration values in ppm were converted to $\mu g\ NO_2/m^3$ by multiplying the ppm value by 1880.

Manual Sample Preparation and Analysis

Absorbing reagent for 3 weeks of operation (15 liters) was prepared and stored in polypropylene carboys. One week's supply of absorption tubes was prepared at the beginning of each week and delivered to the DAMDF for sampling. Polypropylene sampling tubes were scrubbed with soap and water solution and were rinsed with tap water followed by three individual distilled water rinsings. The sampling tubes were segregated by absorbing reagent to dry. Orifice bubblers were cleaned in a 1:3:6 HCl-HNO_3- water solution and rinsed in a distilled water bath followed by forcing distilled water through the bubbler at least three times. The inside diameter of each orifice bubbler was checked with jewelers bits, and only orifice bubblers within 0.35 ± 0.05 millimeter diameter were accepted for the

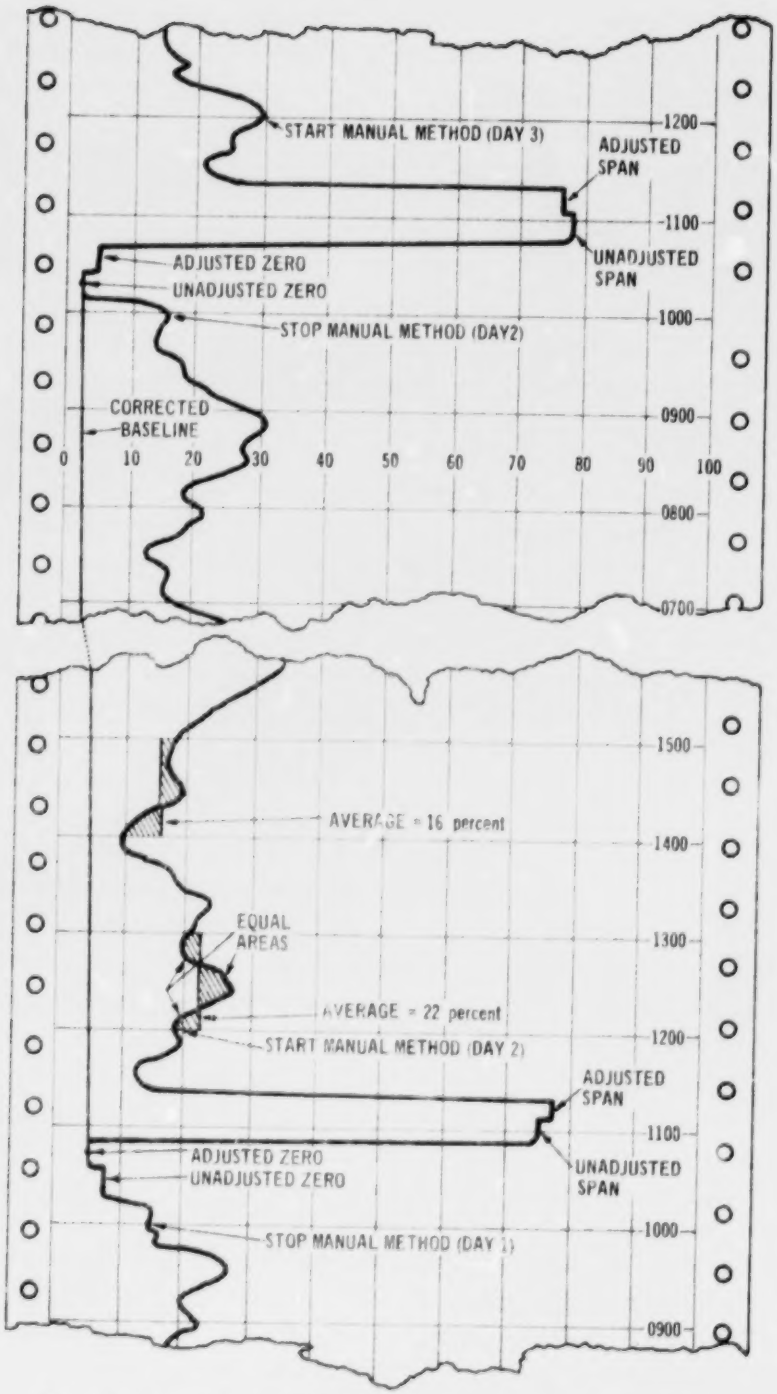

Figure 3. Example of strip chart for chemiluminescence NO_2 analyzer.

study. Assembly of the absorption tubes required adding 50 ml of the respective absorbing reagent, capping the tube, and marking the day, sampler number, and sampler port position on the tube.

The collected bubbler samples were returned weekly to the laboratory for analysis. The absorption tubes were uncapped, the absorbing solution was forced from the orifice bubbler, and each orifice bubbler was rinsed with distilled water. The rinsings plus additional distilled water were added to the collection tube to bring the tube to the original 50-ml volume.

Each week's samples were analyzed in accordance with the procedures given in Appendices A-3 and A-4. Minor modifications to the methods were required. Sulfanilamide solution, coupling reagents (ANSA, NEDA), and nitrite standards were made up in volumes twice that specified in order to conveniently accommodate the large number of samples to be analyzed. The nitrite standard concentrations for both methods were altered to 0.1, 0.2, 0.5, 0.8, 1.0, and 1.4 $\mu g\ NO_2^-/ml$ in order to improve the accuracy of analysis at lower concentrations. Absorbance measurements were made on a Cary 14 spectrophotometer at 540 nanometers (nm).

Nitrogen dioxide concentrations in $\mu g/m^3$ were recorded on data cards, which were initiated when the sample was taken. The date, the sample identification code, the starting and ending time, and the starting and ending flow rates were also recorded on these cards.

QUALITY CONTROL

All of the procedures were subjected to rigorous quality control checks throughout the study. The automated NO_2 analyzers were dynamically zeroed and spanned daily and, if necessary, readjusted to initial calibration conditions. For the duration of the study, unadjusted zero and unadjusted span data were recorded daily, allowing the computation of the zero and span drift data given in Table 2. Critical parameters for each automated method -- such as flow measurements, flow meter readings, vacuum and pressure gauge readings, and span and zero knob settings -- were monitored daily, and observations were recorded on analyzer check sheets. Flow measurements and leak checks were made prior to each sample period using a mass flow meter. Strip chart readings were periodically redetermined by different strip chart readers. Hourly averages were estimated to the nearest $\pm$ 0.005 ppm, and two readers were in agreement within $\pm$ 0.005 ppm. Twenty-two-hour averages determined by two readers were in agreement within $\pm$ 0.002 ppm.

Several routine precautions were taken to assure the integrity of the samples collected by the manual methods. Collection tubes were alternated in the manual gas samplers to minimize any possible manifold effects. Five unknown quality control samples over a 0.20 to 1.40 $\mu g\ NO_2/ml$ range supplied by an independent laboratory were analyzed and determined to be well within the expected variation of each unknown concentration. Reanalysis of 10 percent of the samples demonstrated that the average relative differences between the two analyses for the arsenite

Table 2. ZERO DRIFT AND SPAN DRIFT DATA

	Analyzer[a]				
	CM-1	CM-2	CM-3	C-1	C-2
Zero drift[b]					
Number of recordings	35	34	21	34	34
Minimum value	-33	-10	-2	-17	-5
Maximum value	30	28	1	38	19
Mean	0	3	0	10	3
Standard deviation	8	7	1	12	4
Span drift[c]					
Number of recordings	33	35	20	34	34
Minimum value	-5.4	-4.6	-3.0	-10.7	-6.5
Maximum value	4.8	6.3	4.5	13.1	18.7
Mean	-0.20	0.24	0.22	0.23	1.02
Standard deviation	2.20	2.02	2.27	4.95	4.38

[a] CM-1, CM-2, and CM-3 are chemiluminescence instruments; C-1 and C-2 are colorimetric instruments (see Table 1).

[b] Zero drift = adjusted zero - unadjusted zero ($\mu g\ NO_2/m^3$).

[c] Span drift = $\frac{\text{adjusted span-unadjusted span}}{\text{adjusted span}} \times 100$, at 80 ± 10 percent of full scale.

method was 1 percent with a range of 0 to 3.4 percent; for TGS-ANSA the average was 2.7 percent with a range of 0.18 percent. Absorbance values derived from each standard were compared between analysis periods and within each analysis period; old standards were retained for comparison with newly prepared sets. Sets of five standard solutions covering the analytical range of each method were analyzed at the beginning, middle, and end of each analysis period. Computer-fitted, linear least-squares calibration curves were constructed for each method for each analysis period. A time schedule for addition of sample and reagents was devised in order to minimize the time of the analysis period and to guarantee a consistent time schedule for the analysis of both standards and samples. Thirty-five percent of the samples were reanalyzed by an independent laboratory. The average difference between laboratories was 4 percent for both manual methods throughout the study. One group of shared arsenite method samples differed by 20 percent; however, a close examination of the data generated for that sample period indicated that an anomaly had occurred during the analysis by the independent laboratory.

Two different types of blanks were analyzed with the samples for the purposes of establishing the integrity of the analytical reagents and the absorbing solutions. Analytical blanks were determined by analysis of the stock absorbing solutions at the same time collected samples were analyzed. The TGS-ANSA method analytical blank ranged from 0.005 to 0.020 $\mu g\ NO_2^-$/ml; the arsenite method analytical blank was equal to or less than 0.005 $\mu g\ NO_2^-$/ml. Field blanks were determined by the analysis of the absorbing solution in tubes that were filled, capped, sent to the sampling site, and treated in the same manner as all the absorption tubes except that they were not connected to the sampler.

The field blanks ranged from 0.00 to 0.02 $\mu g\ NO_2^-$/ml and from 0.00 to 0.21 $\mu g\ NO_2^-$/ml for the arsenite and TGS-ANSA procedures, respectively. The TGS-ANSA field blank was lowered to 0.02 $\mu g\ NO_2^-$/ml after extreme measures for cleaning the collecting tubes and caps were taken. Subtracting the TGS-ANSA field blank only disrupted the otherwise excellent agreement between the arsenite and TGS-ANSA data. Considering the good agreement between the TGS-ANSA and the arsenite data without field blank corrections and the fact that a field blank of this type is not required in the TGS-ANSA procedure, field blank corrections were not made.

4. DATA SUMMARIES

Average NO_2 concentrations were computed for each method for each sampling period. The method of computation depended on the method used and has either been discussed in the previous chapter or is included in the method write-up. For convenience in comparing results, all data acquired during the study are presented in this section. Data for each phase are listed separately in Tables 3, 4, and 5. Twenty-two hour NO_2 concentrations obtained by the automated analyzers and by each of the manual methods are given in these tables. Hourly averages were used for the computation of the average NO_2 concentration for the period. Complete data sets from these tables were subjected to statistical analysis. Incomplete sets are included, however, because they provide additional information on the comparability of results produced by some methods.

PHASE I

The average NO_2 concentrations for each of the methods tested are presented in Table 3. The ambient concentrations of NO, CO, CO_2, O_3, TS, and TSP are also given. All data represent concurrent sampling. For each period, two values are given for the continuous automated methods and four values for each of the manual methods. An estimate of total NO_2 concentration, which was obtained by adding the NO_2 addition concentration to the ambient NO_2 measurement, is given for each period. This value is designated as the total concentration. This estimate was not used for determining accuracy of the methods because the gravimetric calibration history of the permeation devices had not been sufficiently established, because of the possibility of reactions of the added NO_2 with unknown constituents in the ambient air, and because the ambient NO_2 measurements were made using one of the NO_2 methods under test. Twenty-two days were required to complete this phase because 2 days were voided because of malfunctions of one or more of the automated analyzers.

TABLE 3. NO_2 METHODS COMPARISON DATA - PHASE I (22-hour averages)
($\mu g\ NO_2/m^3$)

	Ambient Measurements							NO_2 Additions[a]		Methods: Automated				Methods: Manual							
										Chemiluminescence		Colorimetric		Arsenite				TGS-ANSA			
														Sampler A		Sampler B		Sampler A		Sampler B	
Day	TSP	CO[b]	CO_2[b]	TS[c]	O_3	NO	NO_2	Spike	TOTAL	CM-1	CM-2	C-1	C-2	ARS-1	ARS-2	ARS-3	ARS-4	TGS-1	TGS-2	TGS-3	TGS-4
1	136	3.9		28	20	146	103	75	178	173	165	164	164	172	169	180	178	164	160	161	156
2	127	3.3		10	22	125	85	0	85	88	86	81	75	96	94	87	95	92	84	83	81
3	53	6.2	583	5	61	12	34	45	79	73	73	66	62	80	68	75	73	64	50	73	62
4	55	1.4	572	29	26	18	54	83[d]	137	148	152	147	143	146	155	144	150	141	138	136	146
5	154	1.6	702	24	14	242	66	207	273	273	276	274	267	273	262	269	270	274	275	281	271
6	70	1.4	585	8	45	20	58	0	58	58	58	49	47	57	64	66	65	61	63	64	68
7	106	2.4	615	26	20	48	85	207	292	290	288	286	284	275	281	286	286	279	282	282	276
8	66	1.3	601	3	55	2	51	83	134	128	132	147	130	133	137	143	133	128	138	126	126
9	44	2.3	610	5	22	45	58	51	109	102	100	103	98	106	107	109	106	95	100	117	115
10	144	6.9	559	18	16	302	62	51	113	107	109	103	98	129	127	122	126	2.3	112	108	108
11	121	5.6	682	8	22	192	81	94	175	175	179	173	169	184	191	195	198	172	175	187	161
12	50	1.3	593	5	55	2	28	51	79	73	62	94	68	81	75	74	74	74	72	70	74
13	48	1.3	610	0	28	15	36	94	130	128	126	128	132	132	133	141	144	122	122	124	119
14	81	1.6	639	8	12	33	51	0	51	53	49	53	43	52	48	50	53	49	49	46	45
15	51	2.5	586	10	49	1	24	207	231	235	233	252	237	227	220	233	221	219	215	215	226
16	47	1.3	586	8	39	7	34	107[d]	141	147	145	-	-	157	163	160	147	159	162	137	134
17	76	2.1	622	26	16	40	38	102[d]	140	164	165	148	145	156	154	158	161	141	150	144	147
18	89	2.3	617	13	20	59	66	207	273	263	265	261	259	251	249	240	254	240	245	233	247
19	70	1.4	603	24	22	10	56	94	150	150	150	169	147	140	141	143	140	134	138	138	133
20	190	6.4	714	31	16	264	64	102[d]	166	169	147	179	-	170	167	196	187	164	163	160	174
21	123	4.5	646	16	20	130	86	102[d]	188	192	194	197	182	197	193	198	196	173	174	176	189
22	34	1.1	581	0	57	0	17	0	17	17	13	15	8	17	17	17	18	20	21	19	18

[a] Ambient NO_2 measurement (NO_2) plus NO_2 added spike = estimate of NO_2 in sampling manifold (TOTAL).

[b] Milligram/cubic meter (mg/m^3).

[c] Total Sulfur as SO_2.

[d] Resultant from 3-hour addition at 600 to 800 $\mu gNO_2/m^3$.

Table 4. NO_2 METHODS COMPARISON DATA - PHASE II (22-hour averages)

($\mu g\ NO_2/m^3$)

	NO_2			Automated				Manual							
				Chemiluminescence		Colorimetric		Arsenite				TGS-ANSA			
								Sampler A		Sampler B		Sampler A		Sampler B	
Day	Spike[a]	Hours Spiked[b]	Target[c]	CM-1	CM-2	C-1	C-2	ARS-1	ARS-2	ARS-3	ARS-4	TGS-1	TGS-2	TGS-3	TGS-4
1	0	0	0	0	0	0	0	0	0	0	0	5	3	4	4
2	200	22	200	152	150	156	158	162	170	174	167	163	161	137	138
3	733	6	200	201	197	211	209	219	211	221	218	200	200	202	199
4	733	3	100	-	115	117	117	115	120	120	116	109	107	104	108
5	733	3	100	90	90	90	88	95	94	93	97	90	87	89	87
6	733/367	2/2	100	88	92	85	94	98	99	97	98	91	92	89	88
7	275	8	100	79	77	75	85	87	83	88	87	78	76	78	76
8	0	0	0	0	0	0	0	4	3	2	2	6	5	5	5

[a] NO_2 addition concentration.

[b] Hours of NO_2 addition to clean air.

[c] Estimated NO_2 concentration for the 22-hour sampling period.

Table 5. NO_2 METHODS COMPARISON DATA - PHASE III (22-hour averages)

($\mu g\ NO_2/m^3$)

Nitrogen dioxide [a]	Ozone [b]	Automated				Manual							
		Chemiluminescence		Colorimetric		Arsenite				TGS-ANSA			
						Sampler A		Sampler B		Sampler A		Sampler B	
		CM-1	CM-2	C-1	C-2	ARS-1	ARS-2	ARS-3	ARS-4	TGS-1	TGS-2	TGS-3	TGS-4
75	98	66	71	73	64	69	73	72	72	72	70	70	70
	353	66	56	41	34	73	70	71	72	73	72	72	71
	676	78	71	36	32	87	88	85	85	82	82	84	79
150	98	141	130	139	141	152	159	151	155	147	147	145	140
	353	128	120	105	107	142	144	139	140	143	141	141	142
	667	128	128	56	51	141	139	138	138	144	141	144	143

[a] NO_2 added to clean air.

[b] Ozone added to clean air containing NO_2.

PHASE II

The average NO_2 concentrations as measured by each of the four methods under a variety of controlled NO_2 concentration variations are given in Table 4. The data from the manual methods were not corrected for clean air values (days 1 and 8) because no justification for doing so could be found. The NO_2 addition schedule and computed average NO_2 concentration values (target) are also given. As in Phase I, these target values were intended only as an estimate of NO_2 concentrations. The poor agreement between the target values and the measurements by the four NO_2 methods was attributed to a change in rate of one of the permeation tubes used for generation of the NO_2 that was added to the sampling manifold.

PHASE III

The average NO_2 concentrations for each period as determined by the four methods are presented in Table 5. The NO_2 and O_3 concentrations introduced into the sampling manifold for each of the six sampling periods are also listed.

5. STATISTICAL ANALYSIS

The data collected during the study and shown in Tables 3 (Phase I), 4 (Phase II), and 5 (Phase III) were statistically analyzed to provide a basis for comparing both the intramethod and intermethod performances of the four methods. Data analysis consisted of the application of the following statistical procedures: descriptive summaries by method, correlation analysis, multivariate regression analysis, and analysis of variance. Results of these analyses are summarized and presented as: (1) differences (Table 6), (2) cumulative frequency distributions of differences (Table 7), and (3) intermethod ratios by concentration grouping (Table 8).

Table 6 shows the mean difference, the standard deviation about the mean, the 95 percent confidence interval about the mean, and the correlation coefficient for each method and method combination. Determination of statistical significance was based on the observation that the confidence interval did not include zero.

Table 7 shows the distribution of individual daily differences within a specific method and among combinations of methods. For example, the intramethod comparison in Phase I for the chemiluminescence method shows that 90 percent of the differences are 4 $\mu g\ NO_2/m^3$ (0.002 ppm) or less.

Table 8 lists the ratios of the average results of one method compared with the average of another method. The ratios are arranged in concentration intervals from which general observations about concentration effects on the ratios may be easily seen. Each entry in the table is the average of concentration ratios within the interval. For example, the first entry, 1.16, is an average of the two (the number in parentheses) chemiluminescence/colorimetric concentration ratios within the concentration range 0 to 50 $\mu g\ NO_2/m^3$ (0.027 ppm). The last column is the average of all individual ratios across the five concentration intervals.

The general results from the application of these four methods will be discussed below. Details of these statistical analyses, when appropriate, are provided in Appendix B.

Only complete data sets without missing observations for each method for a given sampling period were considered for analysis. In addition, all complete data sets were included in the analysis without regard to outliers. Essentially, the judgment was made that if no valid reason could be found that would justify the elimination of the outlier from the data set, then it must be considered to be representative of the instrument/method capability. Mean differences in approximate percentages may be obtained by dividing the mean difference in $\mu g\ NO_2/m^3$ by the average concentration in Phase I (150 $\mu g\ NO_2/m^3$) and by the average concentra-

Table 6. STATISTICAL ANALYSIS OF METHOD DIFFERENCE ($\mu g/m^3$)

Comparison	Pairs	Mean[a]	Stand Dev.[b]	95% C.I. Lower	95% C.I. Upper	Corr. Coeff.[c]
Phase I						
Chemil/Chemil	22	1.3	5.6	-1.1	3.8	0.999
Color/Color	20	7.5	7.5	3.8	11.3	0.995
AB [illegible] (A)	22	0.6	5.6	-1.9	+3.8	0.997
AB [illegible] (B)	22	0.2	5.6	-1.9	1.9	0.996
TSS/TSS (A)	20	-0.9	3.8	-1.9	.8	0.999
TSS/TSS (B)	22	0.2	9.4	-3.8	+3.8	0.992
[illegible] (B)	22	-2.6	5.6	-5.6	+0.1	0.997
TSS (A)/ TSS (B)	20	0.6	7.5	-3.8	+3.8	0.996
Phase II						
Chemil/Color	7	-4.0	4.6	-8.2	0.3	0.999
Chemil/AB	7	-8.4	6.8	-14.7	-2.1	0.999
Chemil/TSS	7	- .9	2.7	- 3.4	1.6	0.999
Color/AB	8	-4.0	4.9	- 8.1	0.1	0.998
Color/TSS	8	4.0	6.5	- 1.4	9.4	0.998
TSS/TSS	8	8.0	7.9	1.4	14.6	0.999
Phase III						
[illegible]	6	5.2	6.3	-1.4	11.8	0.984
[illegible]	6	3.5	4.6	-1.3	8.3	0.998
[illegible]	6	-1.5	3.7	-5.4	2.4	0.964
[illegible]	6	-1.0	1.5	-2.6	0.6	0.999
[illegible]	6	1.3	1.2	0.0	2.6	0.999
[illegible]	6	1.8	2.6	-0.9	4.5	0.998
[illegible]	6	1.7	1.8	-0.2	3.6	0.999
[illegible]	6	1.3	2.0	-0.8	3.4	0.998
Chemil/Color	6	25.2	28.8	-5.0	55.4	0.730
Chemil/AB	6	-12.3	5.2	-17.8	-6.8	0.995
Chemil/TSS	6	-10.3	5.7	-16.3	-4.3	0.992
Color/AB	6	-37.5	29.8	-67.7	-7.3	0.743
Color/TSS	6	-35.5	32.0	-69.1	-1.9	0.679
TSS/TSS	6	3.3	3.7	- 0.6	7.2	0.985

[a] Signed difference.

[b] Standard deviation.

[c] 95 percent confidence interval of mean difference.

[d] Correlation coefficient between paired values in calculating mean difference.

Table 7. CUMULATIVE FREQUENCY DISTRIBUTIONS OF ABSOLUTE DIFFERENCE BETWEEN DUPLICATE DAILY MEASUREMENTS

($\mu g\ NO_2/3$)

Method	N	Min.	Percentiles									Max.
			10	20	30	40	50	60	70	80	90	
Intramethod												
Phase I												
Chemil	18	0	0	2	2	2	2	2	2	4	4	8
Color	18	0	2	2	4	4	6	6	9	17	23	26
ARS	36	0	2	2	2	4	4	4	6	8	11	13
TGS-ANSA	36	0	0	2	2	4	4	4	6	9	13	90
Phase II												
Chemil	7	0	0	0	0	0	2	2	2	4	4	4
Color	8	0	0	0	0	2	2	2	2	9	10	10
ARS	16	0	0	1	1	1	1	4	4	5	8	8
TGS-ANSA	16	0	0	1	1	1	2	2	2	2	3	4
Phase III												
Chemil	6	0	0	5	5	7	7	8	10	10	11	11
Color	6	2	2	2	2	4	4	5	7	7	9	9
ARS	12	0	0	0	1	1	1	2	3	4	4	7
TGS-ANSA	12	0	0	0	1	1	1	2	2	3	5	5
Intermethod												
Phase I												
Chemil/Color[a]	20	1	3	3	4	4	5	8	8	9	10	18
Chemil/ARS[b]	20	0	1	3	5	6	6	7	8	9	15	18
Chemil/TGS[b]	20	0	1	2	4	5	6	9	10	14	15	23
Color/ARS	20	2	2	3	5	7	8	11	12	15	19	26
Color/TGS	20	0	1	3	5	5	7	8	9	11	19	25
ARS/TGS	20	0	1	2	4	6	7	8	11	15	17	18
Phase II												
Chemil/Color	7	0	0	0	0	0	1	2	2	6	11	11
Chemil/ARS	7	0	0	3	5	5	6	8	8	17	18	18
Chemil/TGS	7	0	0	1	1	1	1	2	2	4	5	5
Color/ARS	7	0	0	3	6	6	6	7	7	8	11	11
Color/TGS	7	0	0	1	3	3	4	5	5	7	10	10
ARS/TGS	7	2	2	4	7	7	8	9	9	17	18	18
Phase III												
Chemil/Color	6	0	0	4	4	18	18	23	40	40	74	74
Chemil/ARS	6	4	4	11	11	11	11	12	18	18	18	18
Chemil/TGS	6	2	2	8	8	8	8	11	15	15	18	18
Color/ARS	6	4	4	14	14	34	34	36	52	52	85	85
Color/TGS	6	2	2	4	4	34	34	36	48	48	89	89
ARS/TGS	6	0	0	0	0	2	2	4	4	4	10	10

[a] Duplicate daily measurements were made by the chemiluminescence and colorimetric methods.

[b] Quadruplicate daily measurements were made by the arsenite and TGS-ANSA methods.

Table 8. INTERMETHOD CONCENTRATION RATIOS BY CONCENTRATION INTERVAL[a, b]

Method	Concentration Interval, $\mu gNO_2/m^3$					
	50	50 - 99	100 - 149	150 - 199	200	Avr.
Phase I						
Chemil/Color	1.16 (2)	1.08(4)	1.00(6)	1.05(4)	1.00(4)	1.04
Chemil/ARS	0.92	0.93	0.96	0.98	1.04	0.97
Chemil/TGS	0.92	1.01	1.03	1.08	1.05	1.03
Color/Chemil	0.86	0.93	1.00	0.95	1.00	0.96
Color/ ARS	0.80	0.88	0.96	0.93	1.04	0.94
Color/ TGS	0.81	0.96	1.03	1.02	1.05	1.00
ARS/Chemil	1.09	1.08	1.04	1.02	0.96	1.03
ARS/Color	1.25	1.14	1.04	1.08	0.96	1.07
ARS/TGS	0.99	1.09	1.07	1.10	1.01	1.06
TGS/Chemil	1.09	0.99	0.97	0.93	0.95	0.97
TGS/Color	1.23	1.04	0.97	0.98	0.95	1.01
TGS/ARS	1.01	0.93	0.93	0.90	0.99	0.94
Phase II						
Chemil/Color	1.00(2)	1.00(3)		0.95(2)		0.99
Chemil/ARS	-[c]	0.92		0.91		0.92
Chemil/TGS	-[c]	1.01		1.00		1.01
Color/Chemil	1.00	1.00		1.05		1.01
Color/ ARS	-[c]	0.93		0.95		0.94
Color/ TGS	-[c]	1.02		1.05		1.03
ARS/Chemil	-[c]	1.09		1.10		1.09
ARS/Color	-[c]	1.08		1.05		1.07
ARS/TGS	-[c]	1.10		1.10		1.10
TGS/Chemil	-[c]	0.99		1.00		0.99
TGS/Color	-[c]	0.98		0.95		0.97
TGS/ARS	-[c]	0.91		0.91		0.91
Phase III						
Chemil/Color		1.59(3)	1.50(3)			1.54
Chemil/ARS		0.88	0.89			0.88
Chemil/TGS		0.91	0.90			0.90
Color/Chemil		0.63	0.66			0.64
Color/ ARS		0.62	0.68			0.65
Color/ TGS		0.64	0.70			0.67
ARS/Chemil		1.13	1.12			1.12
ARS/Color		1.61	1.47			1.54
ARS/TGS		1.03	1.01			1.02
TGS/Chemil		1.10	1.11			1.10
TGS/Color		1.57	1.43			1.50
TGS/ARS		0.97	0.99			0.98

[a] Ratio shown is average of the first method concentration divided by the second method concentration.

[b] Number in parenthesis is number of days within interval.

[c] Ratio is undefined or zero.

tions in Phase II and III (100 µg NO_2/m^3).

PHASE I

Intramethod Comparison

The results of the analysis of data collected during the intramethod variability study of Phase I (Table 3) are summarized in Tables 6 through 8. In all cases, the averages shown are arithmetic averages and the correlations are product-moment correlations.

It can be observed in Table 7 that, in general, each of the methods when used in duplicate under controlled field conditions can yield data that agree remarkably well. Based on the intramethod differences shown in Table 7, the best agreement between duplicate data was shown by the chemiluminescence method followed by the arsenite, TGS-ANSA, and colorimetric methods. The strong degree of association was further evidenced by the fact that the correlation was always better than 0.99. The worst case was shown by the automated colorimetric method. The average differences between 22-hour NO_2 concentration values generated by the two analyzers was 7.5 µg NO_2/m^3 (0.004 ppm), and the 95 percent confidence interval of the mean differences was 3.8 to 11.3 µg NO_2/m^3 (0.002-0.006 ppm). The frequency distribution of absolute differences between duplicate daily measurements given in Table 7 shows that the maximum intramethod difference occurred with the TGS-ANSA method. Although this difference of 90 µg NO_2/m^3 (0.047 ppm), which occurred only once, was considered an outlier, it was not excluded from the analysis because no justification for rejection could be found. Excepting this value, the next highest maximum difference was 26 µg NO_2/m^3 (0.014 ppm), which occurred in the comparison of the continuous colorimetric analyzers.

Intermethod Comparison

A study of the intermethod data (Table 6) showed a statistically significant difference between concentration data produced by the TGS-ANSA and the chemiluminescence methods, with the TGS-ANSA values being lower on the average by 5.6 µg NO_2/m^3 (0.003 ppm). TGS-ANSA method data are also significantly lower than the arsenite method data on the average by 7.5 µg NO_2/m^3 (0.004 ppm). Again the correlations are strongly positive, always above 0.98.

The intermethod comparisons shown in Table 7 indicate that the daily average intermethod differences (based on the median or 50th percentile value) are from 5 to 8 µg NO_2/m^3 (0.003 - 0.004 ppm), which is slightly higher than the intramethod differences of 2 to 6 µg NO_2/m^3 (0.001 - 0.003 ppm). The frequency distributions in Table 7 show that the maximum differences between methods were greater than 20 µg NO_2/m^3 (0.011 ppm) in these cases. These occurred with comparisons of chemiluminescence versus arsenite, chemiluminescence versus TGS-ANSA, and automated colorimetric versus TGS-ANSA.

It can be seen in Table 8 that the average ratio over all concentration intervals is always within ± 10 percent. However, ratios involving colorimetric method concentrations below 50 μg NO_2/m^3 (0.027) differ from the others by as much as 20 percent. Several trends can be seen in Table 8, such as (1) the ratio of the chemiluminescence to arsenite data increases slightly with increasing NO_2 concentration, and (2) all comparisons with the chemiluminescence and colorimetric methods show an increase in ratios with increasing concentration up to 150 μg NO_2/m^3.

The hourly average data produced by the automatic instruments were also examined and are discussed in Appendix B. The concurrent ambient data collected during the study for NO, CO, CO_2, O_3, TS, and TSP were added to a multivariate regression equation to examine the influence of these pollutants on the four NO_2 measurement systems. The analysis showed that these pollutants, at the ambient levels found, did not account for the small differences in results from the various methods. This observation is consistent with the remarkably close agreement among the results produced by the four methods.

PHASE II

The data collected during Phase II (Table 4) were analyzed for effects of variable NO_2 addition on the results produced by the four methods.

Intramethod Comparison

From Table 6 it can be seen that there is a slight bias, amounting to 1.4 μg NO_2/m^3 (0.001 ppm), in the TGS-ANSA sampler A, but this effect is not sufficient to result in a sampler bias for the TGS-ANSA method. Based on duplicate samples (Table 7), the best intramethod agreement is with the chemiluminescence and TGS-ANSA methods, but the arsenite and colorimetric methods are almost as self-consistent. As in Phase I, the correlation coefficients were always above 0.99. Comparing these results with those obtained from Phase I, we find that the two continuous colorimetric instruments yielded results that agreed more closely with each other; so, the instrument bias seen in Phase I was not observed in Phase II. The small bias of 1.4 μg NO_2/m^3 (0.001 ppm) between the two samples from TGS-ANSA sampler A is in contrast to Phase I results, but the practical significance is minimal. In Table 7, a slight intramethod improvement can be noted. This may be attributable to the fact that this portion of the study was run on clean air to which NO_2 had been added instead of ambient air as was used in Phase I.

Intermethod Comparison

Two comparisons, both involving the arsenite method, provided significant data in this phase of the experiment. First, the arsenite method yielded values significantly higher than those produced by the chemiluminescence method by an average of 8.4 μg NO_2/m^3 (0.004 ppm). Similarly the arsenite data were higher than those generated by the TGS-ANSA method by 8.0 μg NO_2/m^3 (0.004 ppm). Based on Phase I results, it is not surprising that the arsenite method produced higher

values than the TGS-ANSA method, but the significant difference between the chemiluminescence and arsenite methods is a surprise because this was not observed in Phase I. Furthermore, it appears, when comparing the mean differences of Phase I with Phase II (Table 6), that the chemiluminescence method behaved more erratically than other methods in Phase II. For example, the mean difference in Phase I with chemiluminescence/colorimetric changed from 3.8 to -4.0 $\mu g\ NO_2/m^3$ (0.002 to -0.002 ppm).

The intermethod differences (Table 7) observed in Phase II are quite similar to those seen in Phase I. All comparisons of data involving the colorimetric method show better agreement in Phase II than in Phase I, not only for the average but also for the maximum differences observed. For example, the chemiluminescence/colorimetric comparison shows a drop from 5 to 1 $\mu g\ NO_2/m^3$ and 18 to 11 $\mu g\ NO_2/m^3$ for the median and maximum, respectively, when Phase I results are contrasted to Phase II results. Again referring to Table 8, it can be seen that the average ratios are all within $\pm$ 10 percent. The ratio comparisons involving the colorimetric method are now all nearer unity.

The detailed procedure for statistically comparing the effects caused by the NO_2 addition procedure on method performance is presented in Appendix B. The analysis shows that the NO_2 addition procedure had an effect. If it can be assumed that a desired concentration can be generated consistently from day to day, then the data from this experiment would indicate that the shorter the NO_2 addition time, the higher the relative results obtained. Perhaps the most significant fact is that each of the four methods behaves similarly to changes in the NO_2 addition procedure. Hence, if there were difficulties in generating a specific NO_2 concentration, all methods reflected this problem.

PHASE III

The data collected during Phase III (Table 5) were analyzed for effects of different concentrations of O_3 on the measurement of NO_2 in a clean air-NO_2-O_3 system.

Intramethod Comparison

No biases between the data generated by any of the methods resulting from the addition of O_3 were observed (see Table 6). Like Phases I and II, the correlation coefficients are always above 0.9 indicating that there is a similarity of response within methods. The data in Table 7 indicate that intramethod differences in Phase III are much like those seen in Phases I and II.

Intermethod Comparison

Whereas in Phases I and II the average mean differences were always less than 10 $\mu g\ NO_2/m^3$ (0.005 ppm), now the intermethod differences are greater than 20 $\mu g\ NO_2/m^3$ (0.011 ppm), in three instances, each occurring when the colorimetric method is compared with other methods. (The colorimetric concentration data are lower than data obtained by the other methods.) In addition, the correlation coefficients in Phase III show less agreement than in Phases I and II. For example,

the chemiluminescence/colorimetric correlation coefficients decreased from 0.99 in in Phase I and II to 0.75 in Phase III. Statistically significant differences are found in four instances, two involving the automated colorimetric method (Color/ARS, Color/TGS-ANSA) and two in which the chemiluminescence method results are compared with others (Chemi/ARS, Chemi/TGS-ANSA).

The intermethod differences shown in Table 7 dramatically demonstrate that high concentrations of O_3 interfered with the performance of the colorimetric methods. Whereas average (median) intermethod differences of 5 to 8 $\mu g\ NO_2/m^3$ (0.003 - 0.004 ppm) were seen in Phases I and II, average differences of 18 to 34 $\mu g\ NO_2/m^3$ (0.01 to 0.018 ppm) can be seen in Phase III data, with a maximum difference of 89 $\mu g\ NO_2/m^3$ (0.047 ppm) between the colorimetric and TGS-ANSA methods.

Referring once again to Table 8, it is obvious that something influenced the performance of the colorimetric method. Whereas on the basis of Phases I and II the ratios might be expected to be somewhere near unity ($\pm$ 10 percent), in Phase III the ratios involving the colorimetric method deviate from the norm by around $\pm$ 50 percent. The statistical analyses comparing the methods (Appendix B) confirm that the colorimetric method differs significantly from the other methods and that the higher the O_3 concentrations, the greater the error introduced. This conclusion is only valid for the commercial version of the colorimetric method tested (Air Monitor IV, Technicon Instruments Corporation). Other commercial versions of this method may or may not exhibit this interference from O_3.

STATISTICAL OBSERVATIONS

The primary observations that result from the statistical analyses are summarized below.

Intramethod Comparisons

The overall agreement within each method throughout all phases of the study is good, as characterized by a mean difference in results from instrument or bubbler pairs of no worse than 7.5 $\mu g\ NO_2/m^3$ (0.004 ppm).

Intramethod data correlations for the four methods are better than 0.95. This means that each method responded similarly to changes in NO_2 concentrations.

A small (<10 percent), but statistically significant, bias exists between the data generated by the two colorimetric instruments.

Fifty percent of the absolute differences between duplicate measurements by any of the four methods is less than 10 $\mu g\ NO_2/m^3$ (0.005 ppm) for each of the four methods.

Intermethod Comparisons

The overall agreement among NO_2 concentration values generated by the different methods is outstanding, as reflected by mean differences of less than 10 $\mu g\ NO_2/m^3$ (0.005 ppm), except when the measurement systems were deliberately challenged by elevated O_3 concentrations (Phase III).

Intermethod data correlations are all better than 0.95 in Phases I and II.

Statistically significant mean differences were observed as follows (Table 6):

1. In Phase I, the TGS-ANSA data were lower than the chemiluminescence data by 5.6 $\mu g\ NO_2/m^3$ (0.003 ppm) and the arsenite data by 7.5 $\mu g\ NO_2/m^3$ (0.004 ppm).
2. The arsenite data were higher than the chemiluminescence data by 8.4 $\mu g\ NO_2/m^3$ (0.004 ppm) in Phase II and by 12.3 $\mu g\ NO_2/m^3$ (0.007 ppm) in Phase III and were higher than the TGS-ANSA data by 8.0 $\mu g\ NO_2/m^3$ (0.004 ppm) in Phase II.

When clear air spiked with both NO_2 and O_3 was analyzed for NO_2, the intermethod mean NO_2 concentration differences of the colorimetric method with respect to those of the other methods were significantly lower at O_3 concentrations of 350 $\mu g/m^3$, indicating that the added O_3 resulted in a negative NO_2 bias for the colorimetric method. Average differences greater than 25 $\mu g\ NO_2/m^3$ (0.013 ppm), over six times those found during the first two phases, were observed.

Fifty percent of the absolute differences between average NO_2 concentrations found by use of the four measurement systems was less than 10 $\mu g\ NO_2/m^3$ (0.005 ppm) for all of the six possible comparisons. However, absolute differences in the colorimetric method data in Phase III were 2 to 3 times higher, that is, 20 to 30 $\mu g\ NO_2/m^3$ (0.011 - 0.016 ppm).

Average concentration ratios of results produced by the four methods for all NO_2 concentration groupings are generally within $\pm$ 10 percent, except in the case of the colorimetric method when challenged with added O_3. In ambient air at the concentration interval of 50 $\mu g\ NO_2/m^3$ (0.027 ppm), ratios involving the colorimetric method differ by as much as 20 percent.

6. REFERENCES

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APPENDIX A - 1.

TENTATIVE METHOD (CHEMILUMINESCENCE PRINCIPLE) FOR CONTINUOUS MEASUREMENT OF NITROGEN DIOXIDE IN ATMOSPHERE

CHEMILUMINESCENCE METHOD

1. Principle and Applicability

1.1 Atmospheric concentrations of nitric oxide (NO) can be measured by the chemiluminescent reaction of ozone (O_3) with NO at reduced or near atmospheric pressure[1]. Nitrogen dioxide (NO_2) is measured as NO in the system after conversion of NO_2 to NO.[2,3] Air samples are drawn directly into the analyzer to establish a NO response; then a switching valve directs the sample air through the converter where the NO_2 is converted to NO. The photomultiplier measures the light energy resulting from the chemiluminescent reactions of NO and O_3. By subtracting the NO signal from the NO+NO_2(NO_x) signal, the amount of NO_2 is determined. The subtractive process is accomplished electronically. Total time for both measurements is less than 1 minute.

1.2 The method is applicable to the measurement of NO_2 at concentrations in the atmosphere ranging from 9.4 to 18,800 $\mu g/m^3$ (0.005 - 10 ppm).

2. Range and Lower Detectable Limit

2.1 A wide variety of ranges can be used in the measurement of NO_2. Recommended ranges are 0 to 376 $\mu g/m^3$ (0 - 0.2 ppm), 0 to 990 $\mu g/m^3$ (0 - 0.5 ppm), 0 to 1,880 $\mu g/m^3$ (0 - 1 ppm), 0 to 3,760 $\mu g/m^3$ (0 - 2 ppm), and 0 to 18,800 $\mu g/m^3$ (0 - 10 ppm). Separate ranges should be made available for NO, NO_2, and NO_x, if possible. These higher ranges are included because NO_x concentrations often exceed 1 ppm.

2.2 The lower detectable limit of the chemiluminescence method for the measurement of NO_2 at the 0 to 376 $\mu g/m^3$ range is 9.4 $\mu g/m^3$ (0.005 ppm).

3. Interferences

3.1 The chemiluminescent detection of NO with O_3 is not subject to interference from any of the common air pollutants, such as O_3, NO_2, carbon monoxide (CO), ammonia (NH_3), or sulfur oxides (SO_x).

3.2 When the instrument is operated in the NO_x mode, any compounds that may be oxidized to NO in the thermal NO_2 converter are potential interferents. The principal compound of concern is ammonia; however, this is not an interferent for converters operated at less than 330°C. Unstable nitrogen compounds, such as peroxyacetyl nitrate (PAN) organic nitrites, decompose thermally to form NO and may represent minor interferences in some polluted atmospheres.

4. Apparatus

4.1 General Description. Most analyzers consist of a particulate filter, a thermal converter[3], an O_3 generator, a reaction chamber, an optical filter, a photomultiplier tube, and a vacuum pump. See Figure A-1 for a general schematic of the chemiluminescence analyzer.

5. Reagents

5.1 Oxygen. A cylinder of extra-dry oxygen is recommended as a source for the generation of O_3.

6. Calibration

6.1 Permeation Tube Method. Atmospheres containing accurately known amounts of NO_2 at levels of interest can be prepared using permeation tubes. In the system for generating these atmospheres, the permeation tube emits NO_2 gas at a known constant rate, provided the temperature of the tube is held constant ($\pm$ 0.1°C) and provided the tube has been accurately calibrated at the temperature of use. The NO_2 gas permeating from the tube is carried by a low flow of dry inert gas to a mixing chamber in which it is accurately diluted with dry NO_2-free air to the level of interest. Systems for the preparation of standard atmospheres have been described in detail by O'Keefe and Ortman[5]; Scaringelli, O'Keefe, Rosenberg, and Bell[6]; and Scaringelli, Rosenberg, and Rehme[7]. Commercial calibration systems using the permeation tube technique are now available.

6.1.1 Preparation of Standard Atmospheres. Permeation tubes may be prepared or purchased. Scaringelli, O'Keefe, Rosenberg, and Bell[6] give detailed, explicit directions for permeation tube calibration. Tube permeation rates from 0.2 to 3.0 micrograms per minute, inert gas flow of about 50 milliliters per minute (ml/min), and dilution flow rates from 1 to 20 liters per minute (liter/min), conveniently give standard atmospheres containing desired levels of NO_2 (9.4 to 1880 $\mu g/m^3$). The concentration of NO_2 in any standard atmosphere can be calculated as follows:

$$C = \frac{P \times 10^3}{R_d + R_1} \qquad \text{(A-1)}$$

where: C = Concentration of NO_2, $\mu g/m^3$ at reference conditions

P = Tube permeation rate, $\mu g/min$

R_d = Flow rate of dilution air, liter/min at reference conditions

R_1 = Flow rate of inert gas, liter/min at reference conditions

6.1.2 Precautions for NO_2 Permeation Tube Use. When using NO_2 permeation tubes the following precautions should be taken:

1. Tubes must be prepared from a pure, dry NO_2 source. Precautions should be taken to assure that condensation is not introduced as the tube is filled.
2. All dilution gases must be clean and dry.
3. Tubes should not be subjected to temperatures above 30°C or below 20°C.
4. Tubes should be stored when not in use in a dry atmosphere with continuous purging with about 50 ml/min of clean dry purge gas (nitrogen or air).
5. The gravimetric calibration of the tube should be carefully checked periodically during the lifetime of tube.

6.2 Gas Phase Titration Method. The gas phase titration method is described in Reference 8.

7. Procedure

7.1 Ambient air sampling is accomplished by following the procedure described in 6.1 The sample is pulled into the instrument by a sample pump or by vacuum from the vacuum pump used in the detector. Ozonized oxygen at a constant flow is drawn into the detector; Figure A-1 shows a typical flow diagram. For exact operating procedures, refer to the manufacturer's instruction manual.

8. Calculation

8.1 Concentrations of NO and NO_2 found in the atmosphere can be obtained by referring directly to the individual calibration curves.

9. References for Appendix A-1

1. Contijn, A., A. J. Sabadell, and R. J. Ronco. Homogeneous Chemiluminescent Measurement of Nitric Oxide with Ozone. Anal. Chem. 42:6, 575, 1970.
2. Hodgeson, J. A., J. F. Bell, K. A. Rehme, K. J. Krost, and R. K. Stevens. Application of a Chemiluminescent Detector for the Measurement of Total Oxides of Nitrogen and Ammonia in the Atmosphere. In: Proceedings of the Joint Conference on Sensing of Environmental Pollutants. Palo Alto, Calif., November 8, 1971. (American Institute of Aeronautics and Astronautics, New York, N. Y.) Paper No. 70-1067.
3. Hodgeson, J. A., K. A. Rehme, B. E. Martin, and R. K. Stevens. Measurements for Atmospheric Oxides of Nitrogen and Ammonia by Chemiluminescence. (Presented at the Air Pollution Control Association Meeting, Miami, June 1972, Paper No. 72-12).
4. Stevens, R. K. and J. A. Hodgeson. Application of Chemiluminescent Reactions to the Measurement of Air Pollutants. Anal. Chem. 45(4):443-449, April 1973.
5. O'Keefe, A. E. and G. C. Ortman. Primary Standards for Trace Gas Analysis. Anal. Chem. 38:760, 1966.
6. Scaringelli, F. P., A. E. O'Keefe, E. Rosenberg, and J. P. Bell. Permeation of Known Concentrations of Gases and Vapors with Permeation Devices Calibrated Gravimetrically. Anal. Chem. 42:871, 1970.
7. Scaringelli, F. P., E. Rosenberg, and K. A. Rehme. Comparison of Permeation Tubes and Nitrite Ion as Standards for the Colorimetric Determination of Nitrogen Dioxide. Environ. Sci. Tech. 4:924-929, 1970.
8. Title 40-Protection of Environment. Tentative Method for the Continuous Measurement of Nitrogen Dioxide. Addendum C - Method for the Calibration of NO, NO_2, and NO_x Analyzers by Gas-Phase Titration. Federal Register. 38(110):15178-15180, June 8, 1973.

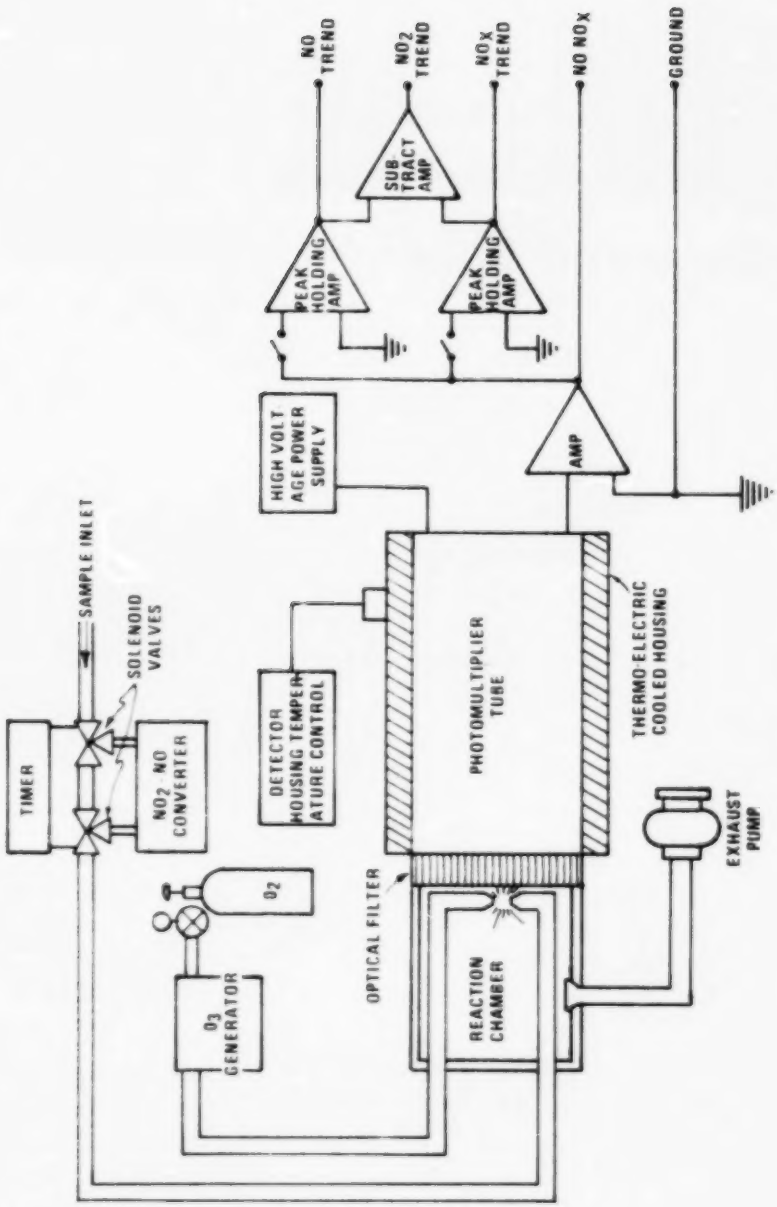

Figure A-1. Automated NO, NO_2, NO_X chemiluminescence analyzer.

APPENDIX A - 2.

TENTATIVE METHOD (COLORIMETRIC PRINCIPLE) FOR CONTINUOUS MEASUREMENT OF NITROGEN DIOXIDE IN ATMOSPHERE

COLORIMETRIC METHOD

1. Principle and Applicability

1.1 This method is based on a specific reaction of nitrite ion (NO_2^-) with diazotizing-coupling reagents to form a deeply colored azo-dye that is measured colorimetrically. The nitrogen dioxide (NO_2) in the ambient air is converted to nitrite ion (NO_2^-) upon contact with an absorbing solution containing the diazotizing-coupling reagents. The absorbance of the azo-dye is directly proportional to the concentration of NO_2 absorbed.

1.2 This method is applicable to the measurement of NO_2 at concentrations in the ambient air from 18.8 to 1880 $\mu g/m^3$ (0.01 - 1 ppm).

2. Range

2.1 A wide variety of ranges is possible. A nominal range of 0 to 80 $\mu g/m^3$ (0 to 1 ppm) with non-linear response is quite common for ambient monitoring. Recently developed instruments are capable of giving linear response in ranges of 0 to 376 $\mu g/m^3$ (0 - 0.2 ppm) and 0 to 940 $\mu g/m^3$ (0 - 0.5 ppm).

3. Interferences

3.1 Interferences from other gases that might be found in the ambient air have been reported to be negligible[1]; however, most interferent studies have been done on manual procedures and may not be applicable to continuous methods. Recent studies indicate that ozone (O_3) produces a negative interference as follows: ratio of NO_2 to O_3 1:1 = 5.5 percent, 2:1 = 19 percent, and 3:1 = 32 percent.

4. Apparatus

4.1 General Description. Sample air is drawn through a gas/liquid contact column at an accurately determined flow rate counter-current to a controlled flow of absorbing reagent. All sample inlet lines prior to the absorber column should be constructed of either glass or Teflon. The absorber must be carefully designed and properly sized because NO_2 is somewhat difficult to absorb. Sufficient time is allowed for full color development; then, the colored solution is passed through a colorimeter in which the absorbance is measured continuously at about 550 nanometers.

4.2 Installation. Instruments should be installed on location and demonstrated, preferably by the manufacturer, to meet or exceed manufacturer's specifications and those described in this method.

4.3 Absorbing Solution. The two most widely used absorbing solutions for this procedure are the Griess-Saltzman[2] reagent and the Lyshkow[3] modification of the Griess-Saltzman reagent. Either of these is acceptable. The composition of these solutions is as follows:

1. Griess-Saltzman. 0.5 gram(g) of sulfanilic acid, 50 milliliters (ml) glacial acetic acid, and 50 ml of 0.1 percent N-(1-napthyl)-ethylene diamine dihydrochloride diluted to 1 liter with deionized water.
2. Lyshkow. 1.50 g of sulfanilamide; 15 g of tartaric acid; 0.05 g of

N-(1-napthyl)-ethylene diamine dihydrochloride; 0.05 g of 2-napthol 3, 6 disulfonic acid disodium salt; and 0.25 ml of Kodak photoflow (as a wetting agent) diluted to 1 liter with deionized water.

5. Calibration

5.1 Permeation Tube Method. Atmospheres containing accurately known amounts of NO_2 at levels of interest can be prepared using permeation tubes. In the system for generating these atmospheres, the permeation tube emits NO_2 gas at a known constant rate, provided the temperature of the tube is held constant ($\pm$ 0.1°C) and provided the tube has been accurately calibrated at the temperature of use. The NO_2 gas permeating from the tube is carried by a low flow of dry inert gas to a mixing chamber in which it is accurately diluted with dry NO_2-free air to the level of interest. Systems for preparation of standard atmospheres have been described in detail by O'Keefe and Ortman[4]; Scaringelli, O'Keefe, Rosenberg, and Bell[5]; and Scaringelli, Rosenberg, and Rehme[6]. Commercial calibration systems using the permeation tube technique are now available.

5.1.1 Preparation of Standard Atmospheres. Permeation tubes may be prepared or purchased. Scaringelli, O'Keefe, Rosenberg, and Bell[5] give detailed, explicit directions for permeation tube calibration. Tube permeation rates from 0.2 to 3.0 micrograms per minute (µg/min), inert gas flow of about 50 milliliters per minute (ml/min), and dilution flow rates from 1 to 20 liters per minute (liter/min) conveniently give standard atmospheres containing desired levels of NO_2 (9.4 to 1880 µg/m^3). The concentration of NO_2 in any standard atmosphere can be calculated as follows:

$$C = \frac{P \times 10^3}{R_d + R} \qquad \text{(A-2)}$$

where: C = Concentration of NO_2, µg/m^3 at reference conditions

P = Tube permeation rate, µg/min

R_d = Flow rate of dilution air, liter/min at reference conditions

R_1 = Flow rate of inert gas, liter/min at reference conditions

5.1.2 Precautions for NO_2 Permeation Tube Use. When using NO_2 permeation tubes the following precautions should be taken:

1. Tubes must be prepared from a pure, dry NO_2 source. Precautions should be taken to assure that condensation is not introduced as the tube is filled.
2. All dilution gases must be clean and dry.
3. Tubes should not be subjected to temperatures above 30°C or below 20°C.
4. Tubes should be stored when not in use in a dry atmosphere with continuous purging with about 50 ml/min of clean, dry purge gas (nitrogen or air.
5. The gravimetric calibration of the tube should be carefully checked periodically during the lifetime of tube.

5.2 Gas Phase Titration Method. The gas phase titration method is described in Reference 7.

5.3 Preparation of Calibration Curve. A series (usually six) of standard atmospheres containing NO_2 levels covering the operating range of the instrument is prepared. Each atmosphere is sampled using exactly the same conditions as will be used during atmospheric sampling. The concentration of NO_2 in micrograms per cubic meter (x - axis) is plotted against instrument response (y - axis), and the line of best fit is drawn.

6. Procedure

6.1 Instrument calibration is described in 5 above. For specific operating instructions, refer to the manufacturer's manual. The instrument should be calibrated dynamically at least once per month. Static calibration checks are recommended daily or at least once per week. Most instruments have a static calibration mode through which sodium nitrite standard solutions can be introduced.

7. Calculations

7.1 The concentration is determined directly from the calibration curve. No calculations are necessary.

7.2 NO_2 concentrations in micrograms per cubic meter are converted to ppm as follows:

$$ppm = \frac{\mu g\ NO_2/m^3}{1880} \qquad \text{(A-3)}$$

(where: 1880 represents the concentration of NO_2 in $\mu g/m^3$ equivalent to 1 ppm NO_2 by volume. The figure was generated for 25°C and 760 mm Hg).

8. References for Appendix A-2

1. Saltzman, B. E. Colorimetric Micro Determination of Nitrogen Dioxide in the Atmosphere. Anal. Chem. 26:1949, 1954.
2. Saltzman, B. E., Modified Nitrogen Dioxide Reagent for Recording Air Analyzers. Anal. Chem. 32:135, 1960.
3. Lyshkow, N. A. A Rapid Sensitive Colorimetric Reagent for Nitrogen Dioxide in Air. J. Air Pol. Control Assoc. 15:10, 481, 1965.
4. O'Keefe, A. E. and G. C. Ortman. Primary Standards for Trace Gas Analysis. Anal. Chem. 38:760, 1966.
5. Scaringelli, F. P., A. E. O'Keefe, E. Rosenberg, and J. P. Bell. Permeation of Known Concentrations of Gases and Vapors with Permeation Devices Calibrated Gravimetrically. Anal. Chem. 42:871, 1970.
6. Scaringelli, F. P., E. Rosenberg, and K. A. Rehme. Comparison of Permeation Tubes and Nitrite Ion as Standards for the Colorimetric Determination of Nitrogen Dioxide. Environ. Sci. Tech. 4:924-929, 1970.

7. Title 40-Protection of Environment. Tentative Method for the Continuous Measurement of Nitrogen Dioxide. Addendum C - Method for the Calibration of NO, NO_2, and NO_x Analyzers by Gas-Phase Titration. Federal Register. 38(110):15178-15180, June 8, 1973.

APPENDIX A - 3.

TENTATIVE METHOD (SODIUM ARSENITE PROCEDURE)

FOR DETERMINATION OF NITROGEN DIOXIDE IN ATMOSPHERE

SODIUM ARSENITE PROCEDURE

1. Principle and Applicability

1.1 Nitrogen dioxide is collected by bubbling ambient air through a sodium hydroxide-sodium arsenite[1] solution to form a stable solution of sodium nitrite. The nitrite ion (NO_2^-) produced during sampling is reacted with phosphoric acid, sulfanilamide, and N-1-(naphthyl) ethylenediamine dihydrochloride to form an azo dye and then determined colorimetrically.

1.2 The method is applicable to the collection of 24-hour samples in the field and their subsequent analysis in the laboratory.

2. Range and Sensitivity

2.1 The range of the analysis is 0.04 to 2.0 μg NO_2^-/ml. Beer's law is obeyed through this range (0 to 1.0 absorbance units). With 50 ml of absorbing reagent and a sampling rate of 200 cm^3/min for 24-hours, the range of the method is 20 to 750 $\mu g/m^3$ (0.01 to 0.4 ppm) nitrogen dioxide[2].

2.2 A concentration of 0.04 μg NO_2^-/ml will produce an absorbance of approximately 0.02 with 1-cm cells.

3. Interferences

3.1 Nitric oxide (NO) is a positive interferent[3]. The presence of NO can increase the NO_2 response by 5 to 15 percent of the NO_2 sampled[2].

3.2 The interference of sulfur dioxide is eliminated by converting it to sulfate ion with hydrogen peroxide before analysis[4].

4. Precision, Accuracy, and Stability

4.1 The relative standard deviations for sampling NO_2 concentrations of 78, 105, and 329 $\mu g/m^3$ are 3, 4, and 2 percent respectively.

4.2 No accuracy data are available.

4.3 Collected samples are stable for at least 6 weeks.

5. Apparatus

5.1 Sampling. A diagram of a suggested sampling apparatus is shown in Figure A-2.

5.1.1 Probe. A Teflon, polypropylene, or glass tube with a polypropylene or glass funnel at the end.

5.1.2 Absorption Tube. Polypropylene tubes, 164-x 32-mm, equipped with polypropylene two-port closures. Rubber stoppers cause high and varying blank values and should not be used. A glass-tube restricted orifice is used to disperse the gas. The tube, approximately 8 mm O.D. and 6 mm I.D., should be 152 mm long with the end drawn out to 0.3 to 0.8 mm I.D.[(a)] The tube should be positioned so as to allow a clearance of 6 mm from the bottom of the absorber.

5.1.3 Moisture Trap. A polypropylene tube equipped with two-port closure. The entrance port of the closure is fitted with tubing that extends to the bottom of the trap. The unit is loosely packed with glass wool to prevent moisture entrainment.

5.1.4 Membrane Filter. A filter of 0.8 to 2.0 micrometers porosity.

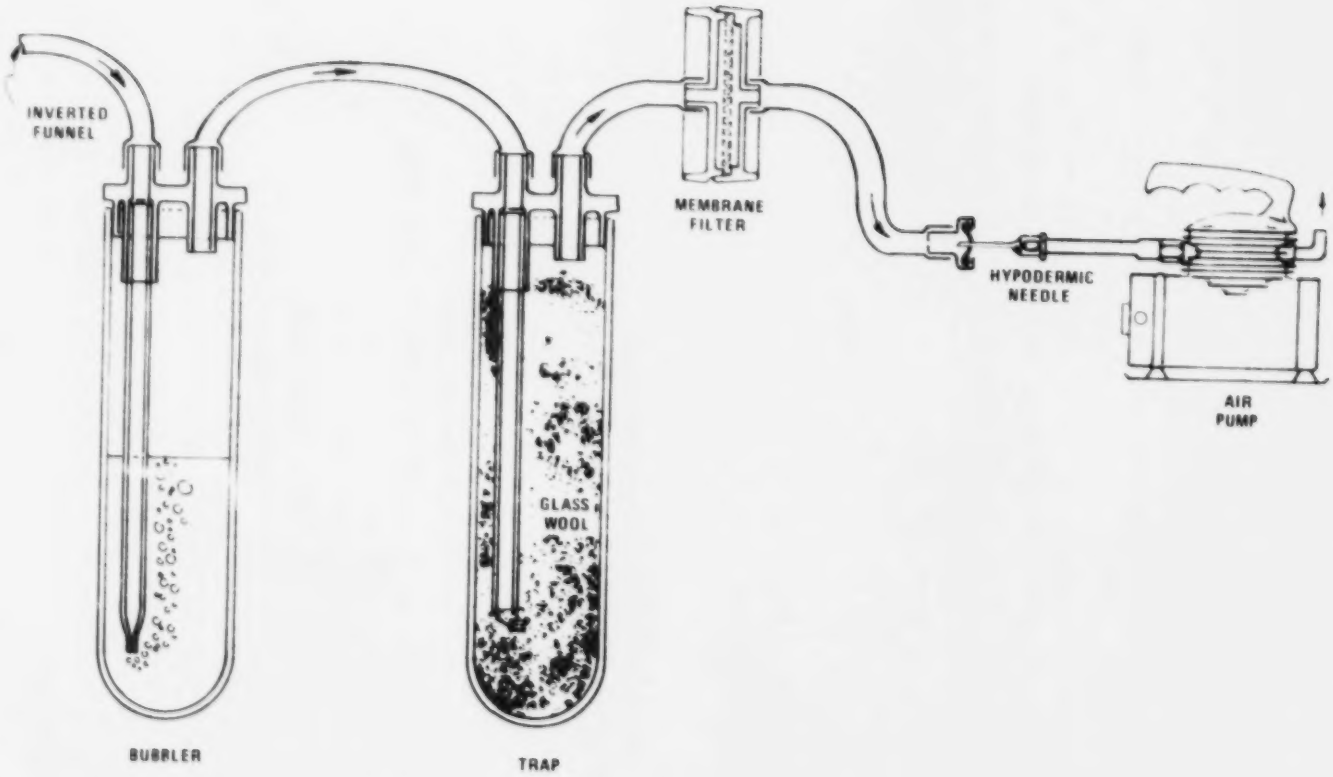

Figure A-2. Sampling train for sodium arsenite procedures.

5.1.5 Flow Control Device. Any device capable of maintaining a constant flow through the sampling solution between 180 and 220 cm^3/min. A typical flow control device is a 27-gauge hypodermic needle,[5] 3/8 inch long. (Most 27-gauge needles will give flow rates in this range.) The device used should be protected from particulate matter. A membrane filter is suggested. Change the filter after collecting 10 samples.

5.1.6 Air Pump. Capable of maintaining a pressure differential of at least 9.6-0.7 of an atmosphere across the flow control device. This value includes the minimum useful differential, 0.53 atmospheres,[5] plus a safety factor to allow for variations in atmospheric pressure.

5.1.7 Calibration Equipment. A flowmeter for measuring airflows up to 275 cm^3/min within $\pm$ 2 percent, a stopwatch, and a precision wet test meter (1 liter/revolution).

5.2 Analysis

5.2.1 Volumetric Flasks. 50, 100, 200, 250, 500, and 1000 ml.

5.2.2 Graduated Cylinder. 1000 ml.

5.2.3 Pipets. 1, 2, 5, 10, and 15 ml volumetric; 2 ml, graduated in 1/10 ml intervals.

5.2.4 Test Tubes, approximately 20 x 150 mm.

5.2.5 Spectrophotometer. Capable of measuring absorbance at 540 nm.

6. Reagents

6.1 Sampling

6.1.1 Sodium Hydroxide. ACS reagent grade.

6.1.2 Sodium Arsenite. ACS reagent grade.

6.1.3 Absorbing Reagent. Dissolve 4.0 g of sodium hydroxide in distilled water, add 1.0 g of sodium arsenite, and dilute to 1000 ml with distilled water.

6.2 Analysis

6.2.1 Sulfanilamide. Melting point, 165-167°C.

6.2.2 N-(1-Naphthyl)-ethylenediamine dihydrochloride (NEDA). Best grade available.

6.2.3 Hydrogen Peroxide. ACS reagent grade, 30 percent.

6.2.4 Sodium Nitrite. Assay of 97 percent $NaNO_2$ or greater.

6.2.5 Phosphoric Acid. ACS reagent grade, 85 percent.

6.2.6 Sulfanilamide Solution. Dissolve 20 g of sulfanilamide in 700 ml of distilled water; add, with mixing, 50 ml of concentrated phosphoric acid; and dilute to 1000 ml. This solution, if refrigerated, is stable for 1 month.

6.2.7 NEDA Solution. Dissolve 0.5 g of NEDA in 500 ml of distilled water. This solution, if refrigerated and protected from light, is stable for 1 month.

6.2.8 Hydrogen Peroxide Solution. Dilute 0.2 ml of 30 percent hydrogen peroxide to 250 ml with distilled water. This solution, if protected from light and refrigerated, may be used for 1 month.

6.2.9 Standard Nitrite Solution. Dissolve sufficient desiccated sodium nitrite and dilute with distilled water to 1000 ml so that a solution containing 1000 μg NO_2^-/ml is obtained. The amount of $NaNO_2$ to use is calculated as follows:

$$G = \frac{1.500}{A} \times 100 \qquad \text{(A-4)}$$

where: G = Amount of $NaNO_2$, grams

1.500 = Gravimetric factor in converting NO_2 into $NaNO_2$

A = Assay, percent

7. Procedure

7.1 Sampling. Assemble the sampling apparatus as shown in Figure A-2. Components upstream from the absorption tube may be connected, where required, with Teflon or polypropylene tubing; glass tubing with dry ball joints; or glass tubing with butt-to-butt joints with tygon, Teflon, or polypropylene. Add exactly 50 ml of absorbing reagent to the calibrated absorption tube (8.1.3). Disconnect the funnel, insert the calibrated flowmeter, and measure the flow before sampling. If the flow rate before sampling is not between 180 and 220 cm^3/min, replace the flow control device and/or check the system for leaks. Start sampling only after obtaining an initial flow rate in this range. Sample for 24 hours and measure the flow after the sampling period.

7.2 Analysis. Replace any water lost by evaporation during sampling by adding distilled water up to the calibration mark on the absorption tube. Pipet 10 ml of the collected sample into a test tube. Pipet in 1 ml of the hydrogen peroxide solution, 10 ml of the sulfanilamide solution, and 1.4 ml of the NEDA solution with thorough mixing after the addition of each reagent. Prepare a blank in the same manner using 10 ml of the unexposed absorbing reagent. After a 10-minute color-development interval, measure the absorbance at 540 nm against the blank. Read μg NO_2^-/ml from the calibration curve (Section 8.2). Samples with an absorbance greater than 1.0 must be reanalyzed after diluting an aliquot (less than 10 ml) of the collected sample with unexposed absorbing reagent.

8. Calibration and Efficiencies

8.1 Sampling

8.1.1 Calibration of Flowmeter. (See Figure 2). Using a wet test meter and a stopwatch, determine the rates of air flow (cm^3/min) through the flowmeter at a minimum of four different ball positions. Plot the ball positions versus the flow rates.

8.1.2 Flow Control Device. The flow control device results in a constant rate of air flow through the absorbing solution. The flow rate is determined in Section 7.1.

8.1.3 Calibration of Absorption Tube. Calibrate the polypropylene absorption tube (Section 5.1.1) by first pipeting in 50 ml of water or absorbing

reagent. Scribe the level of the meniscus with a sharp object, go over the area with a felt-tipped marking pen, and rub off the excess.

8.2 Calibration Curve. Dilute 5.0 ml of the 1000 μg NO_2^- /ml solution to 200 ml with absorbing reagent. This solution contains 25 μg NO_2^- /ml. Pipet 1, 1, 2, 15, and 20 ml of the 25 μg NO_2^- /ml solution into 100-, 50-, 50-, 250-, and 250-ml volumetric flasks and dilute to the mark with absorbing reagent. The solutions contain 0.25, 0.50, 1.00, 1.50 and 2.00 μg NO_2^-/ml, respectively. Run standards as instructed in 7.2, including the blank. Plot absorbance versus μg NO_2^-/ml. A straight line with a slope of 0.42 ± 0.02 absorbance units per μg NO_2^-/ml, passing through the origin, should be obtained.

8.3 Efficiencies. An overall average efficiency of 82 percent was obtained over the range of 40 to 750 μg/m^3 NO_2.

9. Calculation

9.1 Sampling

9.1.1 Calculate volume of air sampled:

$$V = \frac{F_1 + F_2}{2} \times T \times 10^{-6} \qquad \text{(A-5)}$$

where: V = Volume of air sampled, m^3

F_1 = Measured flow rate before sampling, cm^3/min

F_2 = Measured flow rate before sampling, cm^3/min

T = Time of sampling, min

10^{-6} = Conversion of cm^3 to m^3

9.1.2 Uncorrected Volume. The volume of air sampled is not corrected to standard temperature and pressure because of the uncertainty associated with 24-hour average temperature and pressure values.

9.2 Calculate the concentration of nitrogen dioxide as μg NO_2/m^3 using:

$$\mu g\ NO_2/m^3 = \frac{(\mu g\ NO_2/ml) \times 50}{V \times 0.82} \qquad \text{(A-6)}$$

where: 50 = Volume of absorbing reagent used in sampling, ml

V = Volume of air sampled, m^3

0.82 = Collection efficiency

9.2.1 If desired, the concentration of nitrogen dioxide may be calculated as parts per million NO_2 using:

$$ppm\ NO_2 = (\mu g\ NO_2/m^3) \times 5.32 \times 10^{-4} \qquad \text{(A-7)}$$

10. References for Appendix A-3

1. Christie, A. A. et al. Field Methods for the Determination of Nitrogen Dioxide in Air. Analyst. 95:519-524, 1970.
2. Environmental Protection Agency, Research Triangle Park, N. C. 27711, Unpublished results.
3. Merryman, E. L. et al. Effects of NO, CO_2, CH_4, H_2O and Sodium Arsenite on NO_2 Analysis. (Presented at 2nd Conference on Natural

Gas Research and Technology, Atlanta, June 5, 1972.)

4. Jacobs, M. B. and S. Hochheiser. Continuous Sampling and Ultramicrodetermination of Nitrogen Dioxide in Air. Anal. Chem. 30:426, 1958.
5. Lodge, J. P. et al. The Use of Hypodermic Needles as Critical Orifices in Air Sampling. J. Air Pol. Control Assoc. 16:197-200, 1966.

APPENDIX A - 4.

TENTATIVE METHOD (TGS-ANSA PROCEDURE)

FOR DETERMINATION OF NITROGEN DIOXIDE IN ATMOSPHERE

TGS-ANSA PROCEDURE

1. Principle and Applicability

1.1 Nitrogen dioxide (NO_2) collected by bubbling air through a solution of triethanolamine (T), o-methoxyphenol (guaiacol) (G), and sodium metabisulfite (S).[1] The nitrite ion (NO_2^-) produced during sampling is determined colorimetrically by reacting the exposed absorbing reagent with sulfanilamide and 8-anilino-1-naphthalenesulfonic acid ammonium salt (ANSA).

1.2 The method is applicable to the collection of 24-hour samples in the field and subsequent analysis in the laboratory.

2. Range and Sensitivity

2.1 The range of the analysis is 0.025 to 4.0 μg NO_2^-/ml. Beer's law is obeyed throughout this range. With 50 ml of absorbing reagent and a sampling rate of 200 cm^3/min for 24 hours, the range of the method is 20 to 700 μg NO_2/m^3.

2.2 A concentration of 0.025 μg NO_2/ml will produce an absorbance of approximately 0.025 using 1-cm cells.

3. Interferences

3.1 At a NO_2 concentration of 100 $\mu g/m^3$, the following pollutants, at the levels indicated, do not interfere: ammonia, 205 $\mu g/m^3$; carbon monoxide, 154,000 $\mu g/m^3$; formaldehyde, 750 $\mu g/m^3$; nitric oxide, 734 $\mu g/m^3$; phenol, 150 $\mu g/m^3$; ozone, 400 $\mu g/m^3$; and sulfur dioxide, 439 $\mu g/m^3$.

3.2 A temperature of 40°C during collection of sample had no effect on recovery.

4. Precision and Accuracy

4.1 On making measurements from standard nitrogen dioxide atmospheres, prepared by using permeation devices, a relative standard deviation of 2 percent and a collection efficiency of 93 percent were determined throughout the range of the method.

4.2 Stability

4.2.1 The absorbing reagent is stable for 3 weeks before sampling, and the collected samples are stable for 3 weeks after sampling.

5. Apparatus

5.1 Sampling. A diagram of a suggested sampling apparatus is shown in Figure A-3.

5.1.1 Probe. A Teflon, polypropylene, or glass tube with a polypropylene or glass funnel at the end.

5.1.2 Absorption tube. Polypropylene tubes 164-x 32-mm equipped with polypropylene two-port closures. Rubber stoppers cause high and varying blank values and should not be used. A glass tube restricted orifice is used to disperse the gas. The tube, approximately 8 mm O.D. and 6 mm I.D., should be 152 mm long with the end drawn out to 0.3 to 0.6 mm I.D. The tube should be positioned so as to allow a clearance of 6 mm from the bottom of the absorber.

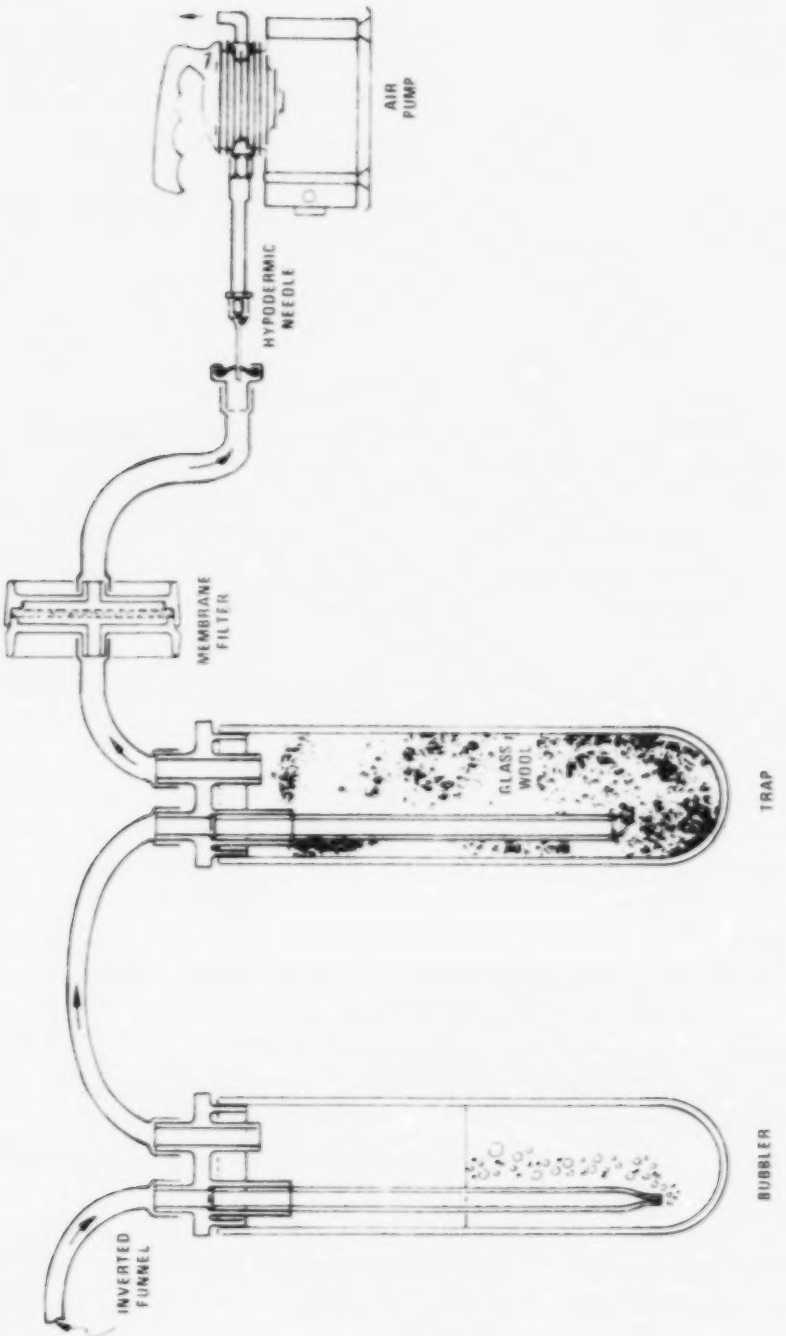

Figure A-3. Sampling train for TGS - ANSA method.

5.1.3 Moisture Trap. A polypropylene tube equipped with a two-port closure. The entrance port of the closure is fitted with tubing that extends to the bottom of the trap. The unit is loosely packed with glass wool to prevent moisture entrainment.

5.1.4 Membrane Filter. A filter of 0.8 to 2.0 micrometers porosity.

5.1.5 Flow Control Device. Any device capable of maintaining a constant flow through the sampling solution between 180 and 220 cm^3/min is acceptable. A typical flow control device is a 27-gauge hypodermic needle,[2] 3/8 inch long. (Most 27-gauge needles will give flow rates in this range.) The device used should be protected from particulate matter. A membrane filter is suggested. Change the filter after collecting 10 samples.

5.1.6 Air Pump. A pump capable of maintaining a pressure differential of at least 0.6 - 0.7 of an atmosphere across the flow control device. This value includes the minimum useful differential, 0.53 atmospheres[2], plus a safety factor to allow for variations in atmospheric pressure.

5.1.7 Calibration Equipment. A flowmeter for measuring airflows up to 275 cm^3/min within $\pm$ 2 percent, a stopwatch, and a precision wet test meter (1 liter/revolution).

5.2 Analysis

5.2.1 Volumetric Flasks. Two 250-ml flasks, two 1000-ml flasks, three 200-ml flasks, seven 100-ml flasks, and one 500-ml flask.

5.2.2 Volumetric Pipets. One each, 2-, 3-, 9-, 10-, 20-, and 50-ml pipets; seven 5-ml pipets.

5.2.3 Serological Pipets. One each 1-, 5-ml pipets graduated in 1/10 ml divisions.

5.2.4 Test Tubes. Each approximately 20 x 150 mm.

5.2.5 Spectrophotometer. Capable of measuring absorbance at 550 nm.

5.2.6 Graduated cylinder. One 50-ml cylinder.

6. Reagents

6.1 Sampling

6.1.1 Triethanolamine [$N(C_2H_4OH)_3$]. Reagent grade.

6.1.2 o-Methoxyphenol ($o\text{-}CH_3OC_6H_4OH$). Also known by its trivial name, guaiacol. Reagent grade. Melting point 27-28°C. (CAUTION: Technical grade material will not meet this specification and should not be used).

6.1.3 Sodium Metabisulfite ($Na_2S_2O_5$). ACS reagent grade.

6.1.4 Absorbing Reagent. Dissolve 20 g of triethanolamine, 0.5 g of o-methoxyphenol, and 0.250 g of sodium metabisulfite consecutively in 500 ml of distilled water. Dilute to 1 liter with distilled water. Mix thoroughly. The solution should be colorless. This solution, if kept refrigerated, is stable for 3 weeks.

6.2 Analysis

6.2.1 Hydrogen Peroxide [H_2O_2]. ACS reagent grade, 30 percent.

6.2.2 Sulfanilamide [4-$(H_2N)C_6H_4SO_2NH_2$]. Melting point 165-167°C.

6.2.3 8-Anilino-1-naphthalenesulfonic acid ammonium salt (ANSA) (8-C_6H_5NH-1-$C_{10}H_6SO_3$-NH_4^+). Minimum analysis, 98 percent.

6.2.4 Sodium Nitrite, [$NaNO_2$]. ACS reagent grade, assay of 97 percent $NaNO_2$ or greater.

6.2.5 Methanol, absolute [CH_3OH]. ACS reagent grade.

6.2.6 Hydrochloric acid, [HCl]. Concentrated. ACS reagent grade.

6.2.7 Hydrogen Peroxide Solution. Dilute 0.2 ml of 30 percent hydrogen peroxide to 250 ml with distilled water. This solution, if protected from light and refrigerated, can be used for 1 month.

6.2.8 Sulfanilamide Solution (2 percent in 4N HCl). Dissolve 2.0 g of sulfanilamide in 33 ml of concentrated HCl and dilute to 100 ml with distilled water. Mix. This solution, if refrigerated, can be used for 2 weeks.

6.2.9 ANSA Solution. 0.1 percent weight per volume (wt/v) Dissolve 0.1 g ANSA in 50 ml of absolute methanol. Dilute to 100 ml with absolute methanol in a volumetric flask. Mix. Keep stoppered when not in use to minimize evaporative losses. Prepare fresh daily. (CAUTION: Older reagent may result in lower absorbance).

6.2.10 Standard Nitrite Solution. Dissolve sufficient desiccated sodium nitrite and dilute with distilled water to 1000 ml to obtain a solution containing 1000 µg NO_2^-/ml. The amount of $NaNO_2$ to use is calculated as follows:

$$G = \frac{1.500}{A} \times 100 \qquad (A-8)$$

where: G = Amount of $NaNO_2$, g

1.500 = Gravimetric factor inconverting NO_2 into $NaNO_2$

A = Assay, percent

7. Procedures

7.1 Sampling. Assemble the sampling apparatus, as shown in Figure A-3. Components upstream from the absorption tube may be connected, where required, with Teflon or polypropylene tubing; glass tubing with dry ball joints; or glass tubing with butt-to-butt joints with tygon, Teflon, or polypropylene. Add exactly 50 ml of absorbing reagent to the calibrated absorption tube (8.1.3). Disconnect the funnel, insert the calibrated flow meter (8.1.1) into the end of the probe, and measure the flow before sampling. Denote rate as F_1. If the flow rate before sampling is between 180 and 220 cm^3/min, replace the flow controlling device and/or check the system for leaks. Start sampling only after obtaining an initial flow rate in this range. Sample for 24 hours and measure the flow after sampling by again inserting a calibrated flowmeter into the probe, after removing the funnel. Denote rate as F_2.

7.2 Analysis. Replace any water lost by evaporation during sampling by

adding distilled water up to the calibrated mark on the absorption tube. Mix well. Pipet 5 ml of the collected sample into a test tube, add 0.5 ml of the peroxide solution, and mix vigorously for approximately 15 seconds. Add 2.7 ml of sulfanilamide solution and mix vigorously for about 30 seconds. Then pipet 3 ml of the ANSA solution; mix vigorously for about 30 seconds. The ANSA solution must be added within 6 minutes of mixing the sulfanilamide solution. (CAUTION: Longer time intervals will result in lowered absorbance values). Prepare a blank in the same manner using 5 ml of unexposed absorbing solution. The absorbance of the blank should be approximately the same as the y-intercept in the calibration curve (Section 8.2). Determine absorbance at 550 nm with distilled water in the reference cell using 1-cm cells. The color can be read anytime from 1 to 40 minutes after addition of the ANSA. Read $\mu g\ NO_2^-$/ml from the calibration curve (Section 8.2).

7.3 Spectrophotometer cells must be rinsed thoroughly with distilled water and acetone, and dried; otherwise a film will build up on the cell walls.

8. Calibration and Efficiencies

8.1 Sampling

8.1.1 Calibration of Flowmeter. (See Figure 2). Using a wet test meter and a stopwatch, determine the rates of air flow (cm^3/min) through the flowmeter at a minimum of four different ball positions. Plot the ball position versus the flow rate.

8.1.2 Flow Control Device. The flow control device provides a constant rate of air flow through the absorbing solution and is determined in 7.1.

8.1.3 Calibration of Absorption Tube. Calibrate the polypropylene absorption tube, (Section 5.1.2) by first pipeting in 50 ml of water or absorbing reagent. Scribe the level of the meniscus with a sharp object, go over the area with a felt-tipped marking pen, and rub off the excess.

8.2 Calibration Curve. Dilute 5.0 ml of the 1000 $\mu g\ NO_2^-$/ml solution to 250 ml with absorbing reagent. This solution contains 20 $\mu g\ NO_2^-$/ml. Dilute 5.0 ml of the 20 $\mu g\ NO_2^-$/ml standard to 200 ml with absorbing reagent. This solution contains 0.50 $\mu g\ NO_2^-$/ml. Prepare calibration standards by pipeting the indicated volume of the standard into volumetric flasks and diluting to the mark with absorbing reagent.

Volume of Standard	Final Volume, ml	Concentration $\mu g\ NO_2^-$/ml
10 ml of 0.50 $\mu g\ NO_2^-$/ml	100	0.05
20 ml of 0.50 $\mu g\ NO_2^-$/ml	100	0.10
2 ml of 20 $\mu g\ NO_2^-$/ml	200	0.20
Use 0.50 μg/ml Standard Directly	-	0.50
5 ml of 20 $\mu g\ NO_2^-$/ml Standard	100	1.00
9 ml of 20 $\mu g\ NO_2^-$/ml Standard	100	1.80

Run standards, plus a blank, as instructed in 7.2. Plot absorbance versus $\mu g\ NO_2^-/ml$. A straight line should be obtained with a slope of approximately 0.50 absorbance units per $\mu g\ NO_2^-/ml$, and a y-intercept (i.e., zero $\mu g\ NO_2^-/ml$) of approximately 0.01 absorbance units. The absorbance is linear up to a concentration of 4.0 $\mu g\ NO_2^-/ml$, absorbance of 1.9. Therefore, if the samples exceed the absorbance of the highest calibration standard and the above absorbance is within the range of the spectrometer, the calibration curve can be extended by including higher concentration standards. If a higher absorbance range is not available, samples must be diluted with absorbing reagent until the absorbance is within the range of the highest standard.

8.3 Efficiencies. An overall average efficiency of 93 percent was obtained from test atmospheres having a nitrogen dioxide concentration of 20 to 700 $\mu g/m^3$.

9. Calculation

9.1 Sampling

9.1.1 Calculate volume of air sampled:

$$V = \frac{F_1 + F_2}{2} \times T \times 10^{-6} \qquad \text{(A-9)}$$

where: V = Volume of air sampled, m^3

F_1 = Measured flow rate before sampling, cm^3/min

F_2 = Measured flow rate after sampling, cm^3/min

T = Time of sampling, min

10^{-6} = Conversion of cm^3 to m^3

9.1.2 Uncorrected Volume. The volume of air sampled is not corrected to standard temperature and pressure because of the uncertainty associated with 24-hour average temperature and pressure values.

9.2 Calculate the concentration of nitrogen dioxide as $\mu g\ NO_2/m^3$:

$$\mu g\ NO_2/m^3 = \frac{(\mu g\ NO_2^-/ml) \times 50}{V \times 0.93} \qquad \text{(A-10)}$$

where: 50 = Volume of absorbing reagent used in sampling, ml

V = Volume of air samples, m^3

0.93 = Overall efficiency of method

9.2.1 If desired, the concentration of nitrogen dioxide may be calculated as ppm NO_2:

$$ppm = (\mu g\ NO_2/m^3) \times 5.32 \times 10^{-4} \qquad \text{(A-11)}$$

10. References for Appendix A-4

1. Mulik, J. D., R. G. Puerst, J. R. Meeker, M. Guyer and E. Sawicki. A Twenty-Four Hour Method for the Collection and Manual Colorimetric Analysis of Nitrogen Dioxide. (Presented at 165th American Chemical Society National Meeting, Dallas, April 8-13, 1973.)

2. Lodge, J. P., Jr., J. B. Page, B. E. Ammons, and G. A. Swanson. The Use of Hypodermic Needles as Critical Orifices in Air Sampling. J. Air Pol. Control Association. 16:197-220, 1966.

APPENDIX B.

STATISTICAL EVALUATION OF METHODS TESTED

PHASE I

Introduction

Concurrent measurements of nitrogen dioxide (NO_2) concentrations in ambient air and in ambient air injected with additional amounts of NO_2 were made over a period of 22 days by the four methods being tested. Duplicate automated instruments (chemiluminescence and colorimetric) were operated, and quadruplicate samples were collected daily for subsequent analysis by each of the two manual methods (arsenite and TGS-ANSA). The daily (22-hour periods beginning at noon) average NO_2 concentrations obtained by the four methods are examined and compared in this section.

Comparison of the methods was based on the determination of difference in bias and the comparison of precision of simultaneous duplicate measurements of NO_2.

In general, we are interested in how well two instruments (or duplicate measurements by a manual method) compare and also in the agreement between concentration data generated under the same conditions by the four methods under test. It is obvious that the terms bias and precision take on specific meanings for this discussion. The best way to convey the meaning of bias and precision is to consider the simultaneous NO_2 measurements as indicated by the quantities:

$$Y_{1i} = \delta_1 + X_i + \epsilon_{1i} \quad \text{(B-1)}$$

$$Y_{2i} = \delta_2 + X_i + \epsilon_{2i} \quad \text{(B-2)}$$

where: $i = 1, 2, \ldots 22$ days.

δ_1 and δ_2 = The biases (unknown) of instruments 1 and 2, respectively, which are made up of drift, calibration error, etc.

X_i = The "true" value (unknown) that is being measured.

ϵ_{1i} and ϵ_{2i} = The random errors (unknown) associated with instruments 1 and 2, respectively. They are composed of measurement errors, the inability of expressions B-1 and B-2 to totally describe a measurement, and other unexplained errors.

For purposes of hypothesis testing, the ϵ_{1i}'s and ϵ_{2i}'s are assumed to be normally and independently distributed of each other and independent of X_i. The assumption of normality is not unreasonable because the measurement errors are composed of a number of individual errors, such as calibration errors, which although possibly not distributed normally as individual observations, tend to be distributed normally as the sum of individual components increases. Before an analysis of the data was made, a plot of the variances of the instruments for each method against the corresponding target value showed that a transformation was not necessary.

The error variance $\sigma^2_{\epsilon_1}$ is a measurement of the precision of instruments 1 and 2, or in other words, a measurement of the closeness of repeated measurements taken by instruments 1 or 2 (or pairs of results obtained using the manual methods). The relative degree of precision attained by an instrument is determined by comparison with other measures of precision on other instruments. For two differ-

ent instruments of the same type, we are interested in $\beta_1 - \beta_2$.

These notions, which conform (by design) to methods given by Grubbs[1], will be employed rigorously in the following analyses.

Analysis of Results

Intramethod Comparisons

Chemiluminescence method- Two identical chemiluminescence instruments were used to make simultaneous NO_2 measurements. To compare the bias (unknown) of the two instruments, we will take advantage of the natural pairing of the measurements resulting from simultaneous readings of a series of 22-hour averages. In doing this, estimates of precision that are free of variability in the day-to-day true (X_i) value can be obtained. This is done by obtaining the difference in the paired measurements by applying the following:

$$V_i = Y_{1i} - Y_{2i} = \beta_1 - \beta_2 + \varepsilon_{1i} - \varepsilon_{2i} \tag{B-3}$$

and then calculating $S^2(V)$, which is an estimate of $\sigma^2_{\varepsilon_1-\varepsilon_2}$. To test the hypothesis that the biases (equal means) are the same (that is, $H_o : \beta_1 = \beta_2$), we calculate.

$$\bar{V} = \sum_{i=1}^{22} V_i = 0.0007 \tag{B-4}$$

$$t = \frac{\bar{V}\sqrt{n}}{S(V)} = \frac{0.0007\sqrt{22}}{0.0029} = 1.163 \tag{B-5}$$

(In this discussion, units are expressed in parts per million. Conversion to $\mu g/m^3$ is made by multiplying ppm by 1880.) This t-value is distributed as a Student's t with 21 degrees of freedom (n-1=21). Comparing t (calculated) with t (theoretical) at $\alpha = 0.05$ level of significance and 21 degrees of freedom, we find that t=1.163 and t (α =0.05, 21 df) = 2.08. [t (theoretical with the corresponding level of significance and degrees of freedom is underscored throughout this appendix to differentiate it from t (calculated).] Therefore, the data are in concordance with the hypothesis that the biases (unknown) are equal. To compare the precision (equal variance) of the two instruments, $\sigma^2_{\varepsilon_1}$ and $\sigma^2_{\varepsilon_2}$, we first find the sum of the paired readings:

$$W_i = Y_{1i} + Y_{2i} = (\beta_1 + \beta_2) + 2X_i + (\varepsilon_{1i} + \varepsilon_{2i}) \tag{B-6}$$

then calculate the correlation coefficient of V and W denoted by r(vw). To test the hypothesis of equal precision ($H_o : \sigma^2_{\varepsilon_1} = \sigma^2_{\varepsilon_2}$) we must calculate:

$$t = \frac{r(VW)\sqrt{n-2}}{[1-r^2(VW)]^{0.5}} = \frac{-0.137502\sqrt{20}}{[1-(-0.137504)^2]^{0.5}} = -0.62 \tag{B-7}$$

This t-value, according to Grubbs, is distributed as Student's t with n-2 = 20 degrees of freedom, resulting in the following expression:
$t = -0.62 \quad > -t(\alpha = 0.05,\ 20\ df) = -2.086$. Therefore, we conclude that the two chemiluminescence instruments are of equal precision in their measurement of NO_2 and that they measured ambient NO_2 with the same bias and precision.

Colorimetric method - The expressions developed in the discussion of the chemiluminescence method also apply here. To determine if there is a difference in the bias (unknown) of the two different colorimetric instruments, we compute t with the aid of formula B-5:

$$t = \frac{\bar{V}\sqrt{n}}{S(V)} = \frac{-0.004\sqrt{20}}{0.004} = -4.472$$

Because this value is less than $-t(\alpha = 0.05,\ 19\ df) = -2.093$, we conclude that there is a significant difference in bias between the two instruments. To determine whether the two instruments have equal precision (that is, $H_0: \sigma\varepsilon_1^2 = \sigma\varepsilon_2^2$) we use formula B-7 to compute:

$$t = \frac{r(W)\sqrt{n-2}}{[1-r^2(W)]^{0.5}} = \frac{(-0.0939)\sqrt{18}}{[1-(-0.0939)^2]^{0.5}} = 0.40$$

and similarly for replicates 3 and 4:

$$t = \frac{(0.025994)\sqrt{20}}{[1-(0.025994)^2]^{0.5}} = 0.115$$

and conclude that both sets of replicates (1 and 2) and (3 and 4) show the same precision of measurement.

The next step is to extend the discussion to compare the average bias of samples 1 and 2 (sampler A) with the average bias of samples 3 and 4 (sampler B). To do so requires calculations using the following expressions:

$$P_i = \frac{(Y_{1i} + Y_{2i})}{2} - \frac{(Y_{3i} + Y_{4i})}{2} = \frac{(\delta_1 + \delta_2)}{2} - \frac{(\delta_3 + \delta_4)}{2} - \frac{(\varepsilon_1 + \varepsilon_2)}{2} - \frac{(\varepsilon_3 + \varepsilon_4)}{2} \quad \text{(B-8)}$$

$$\bar{P} = \frac{\sum_{i=1}^{22} P_i}{n} \quad \text{(B-9)}$$

$$V_i = Y_{3i} - Y_{4i} = (\delta_3 - \delta_4) = (\varepsilon_{3i} - \varepsilon_{4i}) \quad \text{(B-10)}$$

along with estimates of variance S^2 (P) and S^2 (V).

To test the hypothesis that the average bias of samples 1 and 2, $(\delta_1 + \delta_2)/2$, is equal to the average bias of samples 3 and 4, $(\delta_3 + \delta_4)/2$, we calculate another t-value.

$$t = \frac{\bar{P}\sqrt{n}}{S(P)} = \frac{(-0.0014)\sqrt{22}}{0.0035} = -1.876 \quad \text{(B-11)}$$

Because this value is greater than $-t\ (\alpha = 0.05,\ 21\ df) = 2.080$, we conclude that the average bias of arsenite samples from sampler A is the same as the average bias of those from sampler B.

To ascertain whether the average of the variances of sampler 1 and 2, $(\sigma^2_{\epsilon_1} + \sigma^2_{\epsilon_2})/2$ is equal to the average of the variances of samplers 3 and 4, $(\sigma^2_{\epsilon_3} + \sigma^2_{\epsilon_4})/2$, we make a slight departure from Grubb's theory and form the ratio:

$$F = \frac{\frac{(\sigma^2_{\epsilon_1} + \sigma^2_{\epsilon_2})}{2}}{\frac{(\sigma^2_{\epsilon_3} + \sigma^2_{\epsilon_4})}{2}} \qquad \text{(B-12)}$$

which has an F distribution with degrees of freedom for both the numerator and denominator determined according to Satterthwaite[2]. In general, let r denote the desired degrees of freedom for either the numerator or denominator of F. Let r_1 and r_2 denote, respectively, the degrees of freedom for $\sigma^2_{\epsilon_1}$ and $\sigma^2_{\epsilon_2}$. Then:

$$r = \frac{\frac{(\sigma^2_{\epsilon_1} + \sigma^2_{\epsilon_2})}{2}}{\frac{\sigma^4_{\epsilon_1}}{r_1} \quad \frac{\sigma^4_{\epsilon_2}}{r_2}} \qquad \text{(B-13)}$$

In our case, $r_1 = r_2$ and n-1 = 21. Therefore, according to Cochran[3] r lies between 28 and 14. Comparing the calculated F=0.000010/0.000009=1.11 with the theoretical F with numerator degrees of freedom between 28 and 14 and denominator degrees of freedom between 28 and 14, we must conclude that the average variance of measurements 1 and 2 is the same as the average variance of measurements 3 and 4. The range of theoretical F values for $\alpha = 0.05$ and for this range of degrees of freedom is not less than 1.87 nor greater than 2.46.

Comparing this value with $-t\ (\alpha = 0.05,\ 18\ df) = 2.101$, we conclude that the two instruments have equal precision.

Arsenite method - Evaluation and comparison of the manual methods (arsenite and TGS-ANSA) are more involved because quadruplicate samples were collected and subsequently analyzed by each of the two methods to provide the NO_2 data. Duplicate absorption tubes (bubblers) for each of the two manual methods were connected to the manifold in each of the two manually operated gas samplers (sampler A and sampler B). The same expressions (B-1 and B-2) employed in the chemiluminescence section will be used to denote measurements made on arsenite method samples 1 and 2 (sampler A), respectively, and measurements on arsenite samples 3 and 4 (sampler B) by $Y_{3i} = \beta_3 + X_i + \epsilon_{3i}$ and $Y_{4i} = \beta_4 + X_i + \epsilon_{4i}$, respectively. To determine whether arsenite samples 1 and 2 have equal bias, we must use formula B-5 to compute

$$t = \frac{-0.001\sqrt{22}}{0.003} = -0.0156$$

and because this is much greater than $-t\ (\alpha = -0.05,\ 21\ df) = -2.080$, we must conclude that the two samples 3 and 4 were at the same level of bias.

To compare precision between arsenite sample replicates 1 and 2, we compute with formula B-7:

$$t = \frac{(0.016449)\sqrt{20}}{[1-(0.016449)^2]^{0.5}} = 0.073$$

TGS-ANSA method - Expressions developed in the analysis of the arsenite method data also apply in the evaluation of the TGS-ANSA method.

To determine if the biases (unknown) of TGS-ANSA samples 1 and 2 are the same, we use formula B-5 to calculate

$$t = \frac{-0.0005\sqrt{22}}{0.002} = 1.118$$

Likewise, we calculate for samples 3 and 4

$$t = \frac{0.0001\sqrt{22}}{0.005} = 0.089$$

Because neither of these t values is greater than $t\ (\alpha = 0.05,\ 21\ df) = 2.093$, we must conclude that there is no difference in the level of bias for samples 1 and 2, and likewise, no difference in bias for samples 3 and 4. To test the hypothesis that samples 1 and 2 were measured with equal precision ($H_o : \sigma^2_{\epsilon_1} = \sigma^2_{\epsilon_2}$), we use formula B-7:

$$t = \frac{(0.103887)\sqrt{20}}{[1-(0.103887)^2]^{0.5}} = 0.467$$

Also for $H_o : \sigma^2_{\epsilon_3} = \sigma^2_{\epsilon_1}$ we calculate:

$$t = \frac{(-0.014182)\sqrt{20}}{[1.(-0.014182)^2]^{0.5}} = 0.063$$

Because neither of these values fall outside the limits specified by $\pm\ t\ (\alpha = 0.05,\ 20\ df) = \pm\ 2.093$, we must conclude that samples 1 and 2 were measured with equal precision as were those for samples 3 and 4.

To test the hypothesis that the average bias of samples 1 and 2 equals the average bias of samples 3 and 4, we calculate with the aid of formula B-11:

$$t = \frac{0.0003\sqrt{20}}{0.0042} = 0.319$$

Because $t < t\ (\alpha = 0.05,\ 19df) = 2.093$, we must conclude that the averages are equal. Furthermore, to determine whether the results from sampler A on the average have the same precision as those from sampler B, we use formula B-12 to calculate $F = 0.000222/0.000023 = 9.562$.

Because this far exceedes the tabulated F value (which is somewhere between 1.87 and 2.46), we conclude that the results using sampler A do not show the same precision as those from sampler B.

From this analysis, the TGS-ANSA method differs with respect to precision of samples 3 and 4. There is also evidence that the average variances of samples 1 and 2

differ from the average variances of 3 and 4. It is difficult to attribute this to the different manifolds to which these instruments were connected because this was not the case for the arsenite method. As far as bias goes, no differences were found among the TGS-ANSA replicate results.

Intermethod Comparisons - A comparison between methods was made by taking the average of the measurements of instruments (or method) of the same type and comparing these by way of independent t tests. Because the formulas and computations for intermethod comparisons are the same as those applied in the preceding paragraphs, they will not be repeated here. Detailed statistical comparisons of the data generated by the four methods were made following the pattern established for intramethod data analyses.

Summary - The results of the tests for intramethod biases and precision have been presented in detail above and are summarized in Table B-1. A similar summary for intermethod comparisons is presented in Table B-2. The data in Tables B-1 and B-2 indicate that there is a significant difference between the data from the chemiluminescence and TGS-ANSA methods, and between the arsenite and TGS-ANSA methods.

Comparison of Hourly Average Concentrations

The average NO_2 concentrations as determined by the two chemiluminescence instruments ($\overline{CM}$) and the two colorimetric instruments ($\overline{C}$) were calculated for each hour of study period for which data were available. A difference function ($D_m = \overline{CM}-\overline{C}$) was computed and analyzed to assess the agreement between the two methods.

The intermethod differences were averaged on an hour-of-day basis over the study period to see whether any systematic diurnal pattern existed that might be suggestive of "method drift." These averages are shown in Table B-3.

Although these intermethod differences appear to vary systematically with time, the relationship is not of the simple linear form that would be suggestive of a relative linear drift between the two methods. Rather, the difference builds to a positive maximum ($\overline{CM} > \overline{M}$) in midafternoon and then subsides to a relatively constant negative value ($\overline{CM} < \overline{M}$) throughout the evening and morning hours.

Frequency distributions of the entire data set have shown that larger method differences are apt to occur as this NO_2 concentration increases. This apparent tendency may well be confounded with the evidence just seen that method difference is positively correlated with ozone (O_3) concentrations. In order to test this, the cumulative frequency distributions shown in Table B-4 were constructed after deleting the data for hours 10 through 17 when the O_3 concentration is significantly higher.

Table B-1. INTRAMETHOD COMPARISONS - BIAS AND PRECISION

Method	No. of instruments or samples	No. of pairs	r (correlation)	Mean difference[a]	Standard deviation of difference	Null hypothesis (Ho)	t-test[b]	Decision	Conclusion
Chemiluminescence	2	22	0.999	0.0007	0.003	Equal means	1.163	Accept Ho	The chemiluminescence instruments measure with the same level of bias and precision.
						Equal variance	-0.62	Accept Ho	
Colorimetric	2	20	0.995	-0.004	0.004	Equal means	-4.472	Reject Ho	The colorimetric method measures with the same precision but one instrument measures with a bias of 0.004 ppm higher than the other.
						Equal variance	0.40	Accept Ho	
Arsenite Box A	2	22	0.997	0.0003	0.003	Equal means	0.469	Accept Ho	In Box A, the arsenite samples are measured with same level of bias and precision.
						Equal variance	0.214	Accept Ho	
Arsenite Box B	2	22	0.996	-0.001	0.003	Equal means	0.156	Accept Ho	In Box B, the arsenite samples are measured with the same level of bias and precision.
						Equal variance	0.355	Accept Ho	
TGS-ANSA Box A	2	22	0.999	-0.0005	0.002	Equal means	-1.17	Accept Ho	In Box A, TGS-ANSA samples are measured with the same level of bias and precision.
						Equal variance	-0.467	Accept Ho	
TGS-ANSA Box B	2	22	0.992	0.0001	0.005	Equal means	0.093	Accept Ho	In Box B, TGS-ANSA samples are measured with the same level of bias and precision.
						Equal variance	-0.063	Accept Ho	

[a] Signed difference,
[b] Significant at α = 0.05 significance level.

Table B-2. INTERMETHOD COMPARISONS - BIAS

Methods	No. of instruments or samples	No. of pairs	Mean difference[a]	Standard deviation of difference	Null hypothesis (Ho)	t-test[b]	Decision	Conclusion
Chemiluminescence versus Colorimetric	2	20	0.0016	0.0039	Equal means	1.844	Accept Ho	Chemiluminescence and colorimetric methods measure with equal levels of bias.
Chemiluminescence versus Arsenite	2	20	-0.0014	0.0050	Equal means	-1.231	Accept Ho	Chemiluminescence and arsenite methods measure with the same level of bias.
Chemiluminescence versus TGS-ANSA	2	20	0.0050	0.0047	Equal means	2.654	Reject Ho	Chemluminescence bias level exceeds the TGS-ANSA bias level by 0.0020 ppm.
Colorimetric versus Arsenite	2	20	0.0003	0.0062	Equal means	0.207	Accept Ho	Colorimetric and Arsenite methods measure with the same level of bias.
Colorimetric versus TGS-ANSA	2	20	0.0033	0.0056	Equal means	2.660	Accept Ho	Colorimetric and TGS-ANSA methods measure with the same level of bias.
Arsenite versus TGS-ANSA	2	20	0.0039	0.0037	Equal means	4.719*	Reject Ho	Arsenite bias level exceeds TGS-ANSA bias level by 0.0039 ppm.
Arsenite (A)	2	20	-0.0014	0.0035	Equal means	-1.670	Accept Ho	Arsenite bias level in sampler A is equal to arsenite bias level in sampler B.
Arsenite (B)	2							
TGS-ANSA (A)	2	20	0.0004	0.0042	Equal means	0.319	Accept Ho	TGS bias level in sampler A is equal to TGS bias level in sampler B.
TGS-ANSA (B)	2							

[a]Signed differences, ppm.

[b]Significant at the α=.05 significant level.

Table B-3. DIURNAL PATTERN OF INTERMETHOD DIFFERENCES [a]

Hr	D_m	Hr	D_m	Hr	D_m	Hr	D_m
1	-1.5	7	-2.1	13	+9.2	19	+1.3
2	-3.0	8	+0.4	14	+8.8	20	+0.8
3	-2.1	9	+1.1	15	+16.5	21	+1.1
4	-3.2	10	+8.6	16	+19.0	22	+0.4
5	-3.2	11	Calibrate	17	+15.8	23	-0.4
6	-0.9	12	Calibrate	18	+5.6	24	-1.1

[a] $D_m = \overline{CM} - \overline{C}$

Table B-4. CUMULATIVE FREQUENCY DISTRIBUTION OF HOURLY INTERMETHOD DIFFERENCES BY CONCENTRATION GROUPING
(Percent)

NO_2 concentration, $\mu g/m^3$	Range of D_m [a], $\mu g/m^3$		
	≤9	≤19	≤28
<94	87.9	100	100
94-188	94.2	98.9	100
188-282	82.1	100	
>282	100		
	98.4	99.7	100

[a] $D_m = \overline{CM} - \overline{C}$.

On the basis of the foregoing it appears that in this case the inter-method ($\overline{CM}$-$\overline{C}$) difference is not dependent on NO_2 concentration, but is, rather, a direct function of O_3 concentration, an inverse function of nitric oxide (NO) concentration, or some combination of both O_3 and NO.

In an attempt to find possible explanations for the above observation, diurnal NO, NO_2, and O_3 concentrations were plotted (Figure B-1). Data were not recorded for hours 11 and 12 during the study period because this time interval was used each day to calibrate instruments and to perform other tasks in preparation for the following 22-hour sampling period. For the majority of the days in the study period, either no NO_2 or a constant-level NO_2 spike was administered over the course of the day, which accounts for the constant difference between ambient NO_2 and the total NO_2 curves during the morning and evening hours. On 5 of the 21 days, a 3-hour NO_2 spike was administered (from hour 13 to 16 or hour 14 to 17), which accounts for the mid-day peak in total NO_2.

The difference between the chemiluminescence and colorimetric hourly averages ($\overline{CM}$-$\overline{C}$) between 1300 and 1900 hours when the ambient O_3 concentrations are highest indicates that colorimetric NO_2 values are indeed depressed by the higher levels of O_3 in the atmosphere. However, the situation is somewhat clouded by the fact that the 3-hour spiking also was performed during this portion of the day and this spiking itself might be responsible for the greater D_m.

To separate the possible effects of 3-hour NO_2 spiking from those caused by O_3, the diurnal averages were recalculated after deleting data for those 5 days when 3-hour NO_2 spiking was done. These results appear in Figure B-2. Now the curves for total NO_2 follow the ambient curve very closely; the near constant difference being the result of a uniform (day-long) spiking rate. The amount that the chemiluminescence method values exceeded those of the colorimetric method is shown as the shaded area on the upper graph.

In Figure B-3, the hourly average method differences are plotted against the hourly average concentrations of O_3 and NO. The correlation coefficients of NO_2 intermittent differences (D_m) with O_3 and NO are + 0.87 and -0.78, respectively. This supports the hypothesis that there is a negative interference of O_3 and a positive interference of NO with the colorimetric NO_2 method.

Effects of Other Ambient Pollutants

A multiple regression equation that incorporates the concurrent ambient data collected on six common pollutants (independent variables) -- total suspended particulate matter (TSP), carbon monoxide (CO), carbon dioxide (CO_2), total sulfur (TS), ozone (O_3), and nitric oxide (NO) -- was developed. Another variable, the NO_2/O_3 ratio, was added. These data were incorporated into a linear model to find answers to the following questions:

1. Will including these data improve the comparability of a method so

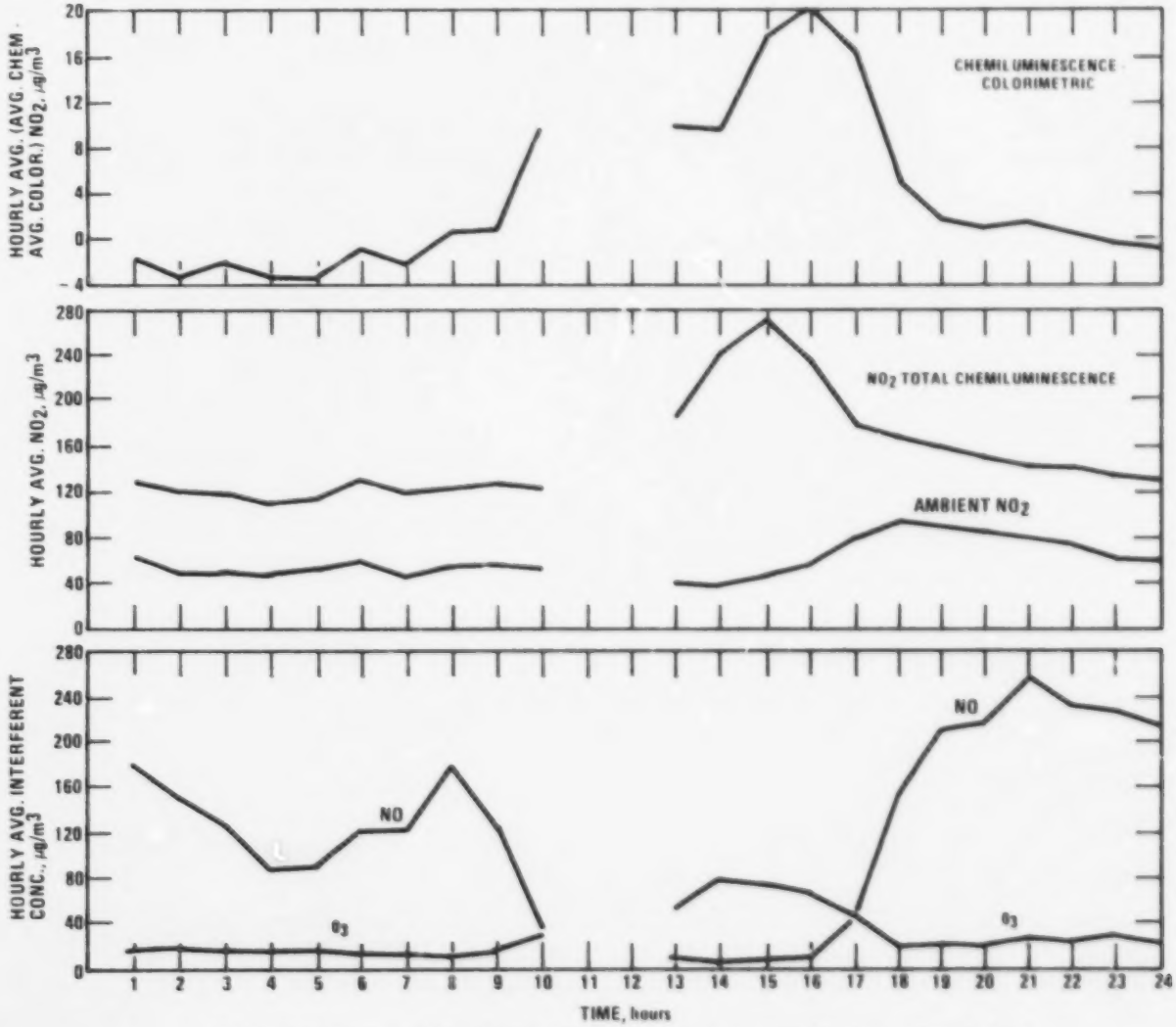

Figure B-1. Phase I - NO_2 methodology study - hourly averages for continuous methods.

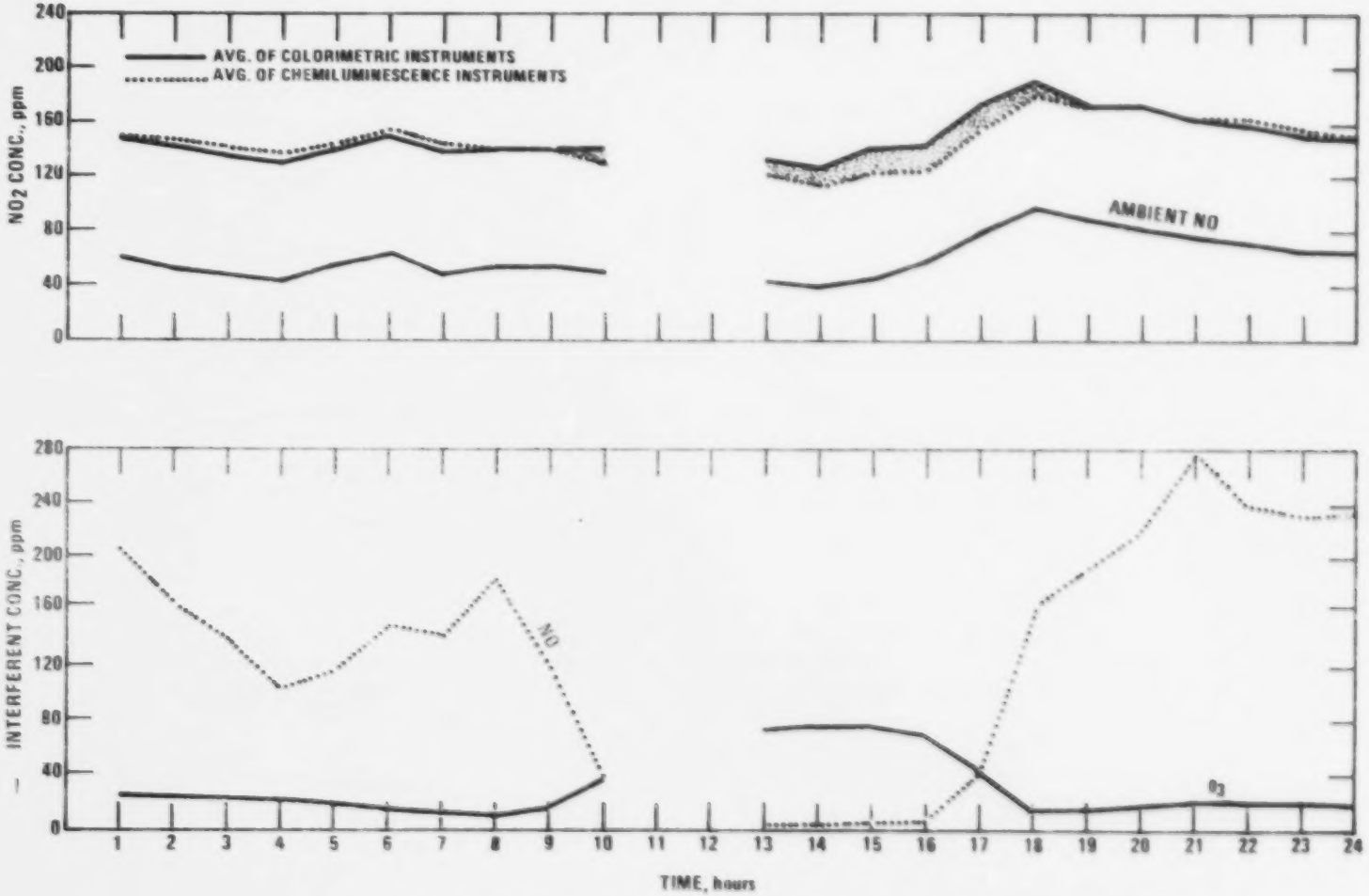

Figure B-2. Phase I - diurnal patterns (excluding intermittent spike days).

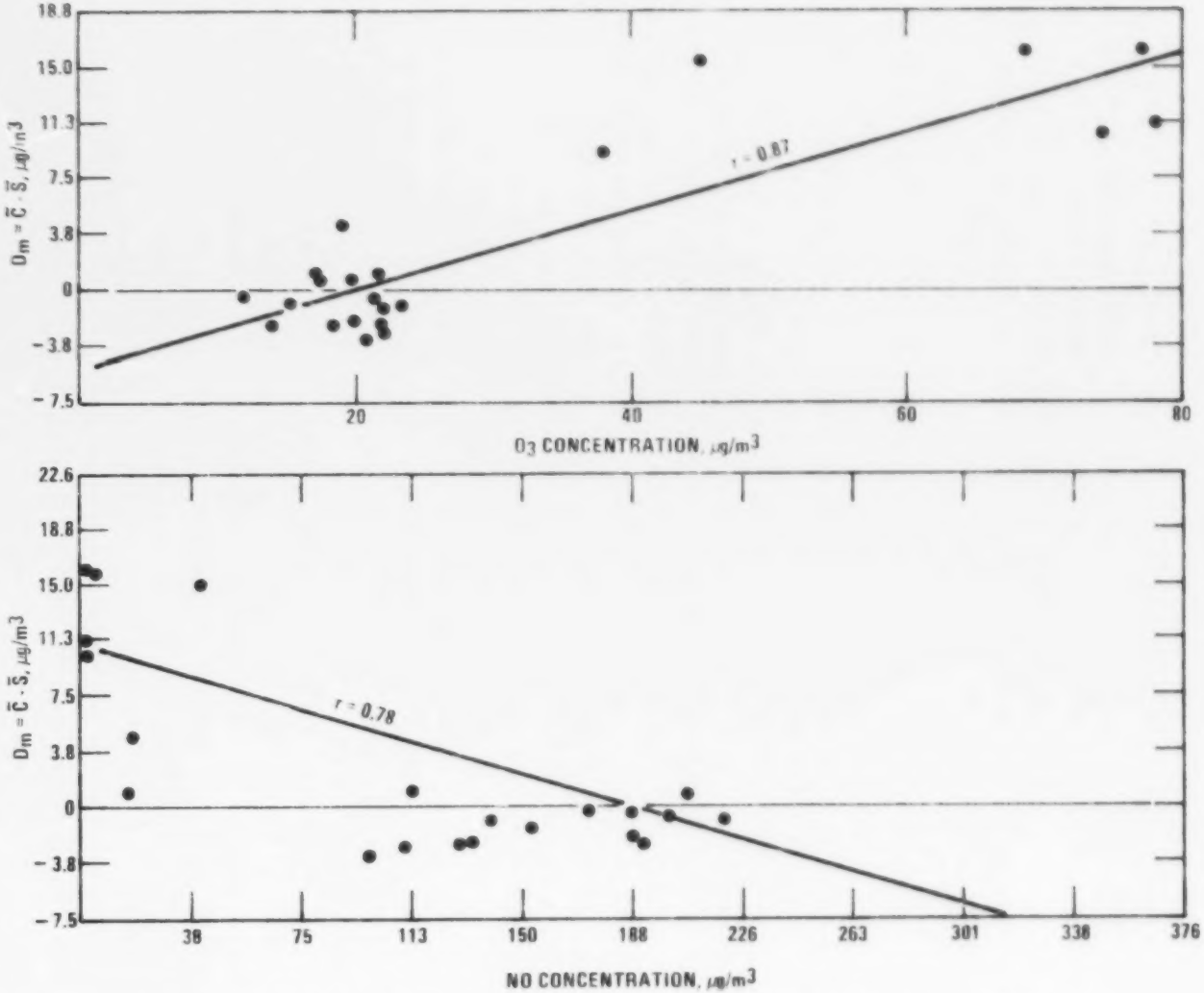

Figure B-3. Method difference versus interferent concentrations (excluding intermittent spike days).

that the response is now closer to the true (target) value?

2. Will including these data improve the inter-relatability of the four methods? Thus, if one could adjust the measurements made by one method, the effect caused by O_3, for example, and thereby improve the intermethod agreement, then it can be concluded that the results from one method relative to another are affected (interfered with) by that pollutant.

Analysis of Data -In answer to the first question, 22-hour concentrations were averaged over the number of instruments or analyses for each method for each day. For example, the 22-hour averages from the two chemiluminescence instruments were averaged and that one result was taken as the estimate of NO_2 concentration for that day for that method. Similarly one average for each day was recorded for the colorimetric method (2), arsenite method (4), and TGS-ANSA method (4). Each method average was then subtracted from the target NO_2 value for the day. This array of differences was then considered as the dependent variable by which the data from the independent variables were to be added in an attempt to "explain" this residual difference.

The analysis of variance table (Table B-5) in all cases indicates that the F value for the overall regression equation is not significant. This means that the independent variables could not significantly account for any variability in the dependent variable. It can be observed that the best fit with added variables (as measured by R^2) is for the colorimetric method (nearly 50 percent of the variation). The largest coefficient for all methods except the chemiluminescence method is associated with the CO_2 variable. (CO is second to the TS variable for the chemiluminescence method).

A similar procedure was followed for testing the inter-relatability of data obtained by each of the methods. In order to derive the dependent variable array, differences between method averages were calculated for each day. The equation incorporating independent variables was fitted to this array of differences through step-wise multiple regression techniques.

The analysis of variance table (Table B-6) in all cases indicates that the F value for the overall regression equation is also not significant. This affirms the conclusion that the independent variables could not significantly account for any variability in the array of differences between methods. It can be observed that the best fit with added variables (based on R^2 values) involves the chemiluminescence/arsenite methods.

However, even in this best case comparison, only 37 percent of the variation is explained. Consistent with Table B-5 results, the largest coefficient for all models, that is, all comparisons, is associated with CO_2. However, this variable is still not significant in any of the models, nor are any of the other variables. Therefore, the overall conclusion must be that, during Phase I at the ambient (22-hour average) levels of the pollutants measured concurrently with NO_2, no significant interferences were detected.

Table B-5. ANALYSIS OF VARIANCE - DIFFERENCE FROM TRUE (ppm)[a]

Measurement method	Source	Sequential F value	B values	T for Ho: B=0	Standard error of B	Overall significance of regression equation F	R^2
Chemiluminescence	NO	0.03	0.030	- 0.48	0.063	1.095	0.34
	CO_2	0.18	-0.047	- 0.24	0.196		
	O_3	2.21	0.002	0.08	0.020		
	TS	3.96	-0.068	- 2.03	0.034		
	CO	0.05	-0.001	0.15	0.006		
	Ratio	0.14	-0.000	0.37	0.0001		
	Intercept	-	+0.018	0.26	0.067		
Colorimetric	NO	1.68	0.083	1.32	0.063	1.547	0.46
	CO_2	1.07	-0.263	- 1.33	0.198		
	O_3	0.08	-0.028	- 1.41	0.020		
	TS	4.56	-0.063	- 1.72	0.037		
	CO	1.11	0.010	1.23	0.008		
	Ratio	0.79	0.000	0.89	0.001		
	Intercept	-	0.092	1.35	0.068		
Arsenite	NO	2.22	0.024	0.23	0.105	0.460	0.18
	CO_2	0.04	-0.149	- 0.46	0.326		
	O_3	0.15	-0.010	- 0.29	0.034		
	TS	0.07	-0.019	- 0.34	0.057		
	CO	0.11	-0.005	- 0.40	0.014		
	Ratio	0.16	-0.000	- 0.40	0.0002		
	Intercept	-	0.054	0.48	0.112		
TGS-ANSA	NO	3.44	-0.007	- 0.08	0.086	1.180	0.35
	CO_2	0.17	-0.119	- 0.44	0.269		
	O_3	1.67	-0.029	- 1.04	0.028		
	TS	0.21	-0.034	- 0.72	0.047		
	CO	0.06	-0.034	- 0.02	0.011		
	Ratio	1.53	-0.000	- 1.24	0.000		
	Intercept	-	0.051	0.55	0.092		

[a]Units of ppm apply to B Values and the standard of B. Other values are unitless.

Table B-6. ANALYSIS OF VARIANCE - METHOD DIFFERENCE (ppm)[a]

Correlation value	Source	Sequential F value	Coefficient	t-Test	Standard error of b	Overall significance of regression equation	
[illegible]	[illegible]						
	WD	0.02	0.56	0.14	0.079	0.400	0.54
	WD^2	0.13	-0.117	-0.36	0.041		
	T_D	1.65	0.0079	0.39	1.020		
	T_D^2	1.41	0.004	0.37	0.043		
	CO	0.22	0.060	0.47	0.010		
	Ratio	0.01	-0.000	-0.10	0.0004		
	Intercept	-	-0.060	-0.44	0.094		
[illegible]							
	WD	1.23	0.086	.40	0.067	0.905	0.37
	WD^2	0.13	-0.060	-0.36	0.272		
	T_D	1.25	0.0074	0.35	1.020		
	T_D^2	.96	0.004	.14	1.047		
	CO	0.22	-0.060	-0.46	0.011		
	Ratio	0.03	-0.000	-0.40	0.0005		
	Intercept		0.060	0.44	0.093		
[illegible]							
	WD	.58	-0.205	-0.75	0.118	0.720	0.37
	WD^2	0.54	0.230	0.68	1.054		
	T_D	0.35	0.0033	0.16	0.034		
	T_D^2	0.30	0.001	0.34	0.003		
	CO	0.30	-0.013	-0.41	0.014		
	Ratio	0.01	-0.004	-0.35	0.0006		
	Intercept		0.014	0.32	0.121		
[illegible]							
	WD	0.41	-0.052	-0.42	0.126	0.422	0.22
	WD^2	0.43	0.133	0.31	0.392		
	T_D	0.43	0.004	0.17	0.031		
	T_D^2	0.31	0.029	0.43	0.064		
	CO	0.02	-0.011	-0.08	0.016		
	Ratio	0.02	-0.000	-0.14	0.0007		
	Intercept	-	-0.040	-0.30	0.135		
[illegible]							
TSS-TDS	WD	1.33	-0.141	-1.05	0.137	0.900	0.37
	WD^2	2.13	2.409	0.36	6.427		
	T_D	0.23	0.004	0.09	0.041		
	T_D^2	0.17	0.021	0.29	0.074		
	CO	0.04	-0.015	-0.90	0.017		
	Ratio	0.01	-0.000	-0.08	0.0009		
	Intercept	-	-0.132	-0.91	0.145		
[illegible]							
TDS-TSA	WD	0.44	-0.091	-1.14	0.079	0.515	0.26
	WD^2	2.20	0.285	1.16	0.248		
	T_D	3.20	5.008	0.34	0.024		
	T_D^2	0.03	-0.008	-0.19	0.043		
	CO	0.22	-0.005	-0.47	0.010		
	Ratio	0.01	-0.000	0.10	0.0004		
	Intercept	-	-0.092	-1.09	0.084		

[a]Units of ppm apply only to D values and the standard error of D. Other values are unitless.

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PHASE II

Introduction

In Phase II, NO_2 measurements were made using four different NO_2 measurement methods. In this phase, the NO_2 being measured had been added to a clean air system at three fixed levels -- 0 $\mu g\ NO_2/m^3$ (clean air), 100 $\mu g\ NO_2/m^3$ and 200 $\mu g\ NO_2/m^3$. The NO_2 levels were varied according to a predetermined addition schedule. To analyze the data, a nested factorial experimental design was assumed. The tree diagram given in Figure B-4 gives the underlying design of the experiment.

Figure B-4. Phase II - Design of experiment.

In the analysis, each different type of instrument (or manual method) was considered as giving a replicate measurement for that particular method. The purpose of the analysis was to compare different methods on the basis of their abilities to measure different levels of NO_2 in clean air.

Analysis of Results

An analysis of variance was performed with subsequent tests of hypotheses about the underlying model

$$Y_{ijkl} = \mu + M_i + N_j + MN_{ij} + SN_{k(j)} + \epsilon_{l(ijk)} \qquad (B\text{-}14)$$

where: Y_{ijkl} = The l^{th} NO_2 measurement by the i^{th} method on the j^{th} NO_2 level administered according to the k^{th} schedule

μ = A constant appearing in all measurements

M_i = The effect of the i^{th} method on the measurement

N_j = The effect of the j^{th} NO_2 level on the measurement

MN_{ij} = The combined effect of the i^{th} method and the j^{th} level of NO_2

$SN_{k(j)}$ = The spiking schedule for a certain NO_2 level (nested effect) on the measurement

$\epsilon_{l(ijk)}$ = The random error of measurement

For purposes of hypothesis testing, the $\epsilon_{l(ijk)}$'s are assumed to be normally and independently distributed about zero and with constant variance. Results of this analysis are presented in Table B-7.

Table B-7. ANALYSIS OF VARIANCE - PHASE II

Source	DF[a]	Sum of squares	Mean square	F
Method	3	0.00040238	0.00013412	27.21
NO_2	2	0.11012932	0.05550646	11,222.30
Method x NO_2	6	0.00027575	0.000045958	10.06
Schedule (NO_2)	4	0.00593331	0.00148333	30.09
Error	79	0.0003399	0.00000493	
Total	94	0.11518236		

[a]DF = degree of freedom.

All F values were significant at the $\alpha = 0.01$ level; consequently, the hypothesis was rejected.

Using Duncan's Multiple Range Test (Table B-8), the means are ranked from the lowest to highest. Any two means shown that are not underscored by the same line are significantly different.

Table B-8. SUMMARY OF DUNCAN'S TEST - PHASE II

Methods:[a]	CM	TGS	COLOR	ARS
Means:	88.2	90.2	92.7	98.1

NO_2	C-0	S-0	A-0	T-0	C-100	T-.05	S-100	A-200	T-200	C-200	S-200	A-200
	0.0	0.0	1.3	4.9	88.9	90.6	93.8	99.3	174.8	175.4	183.3	192.5

Schedule (NO_2)	1A (0.0)	3D (100)	3B (100)	3C (100)	3A (100)	2A (200)	2B (200)
Means:	2.1	89.7	91.4	91.9	113.0	157.4	207.2

[a]Chemiluminescence (CM), TGS-ANSA (TGS), colorimetric (COLOR), arsenite (ARS).

Conclusions

The results of Duncan's Test indicate that, on the average, a significantly higher ($\alpha = 0.05$) reading was given by the arsenite method as compared with those of the chemiluminescence, colorimetric, and TGS-ANSA methods, which gave essentially the same readings. At the 0 $\mu g\ NO_2/m^3$ level, the average chemiluminescence, colorimetric, and arsenite readings did not differ significantly ($\alpha = 0.05$). However, each of these methods gave readings that differed significantly from those given by the TGS-ANSA method. At the 100 $\mu g\ NO_2/m^3$ level, the colorimetric and arsenite methods, on the average, gave the same

results but both gave significantly higher results than either the chemiluminescence or the TGS-ANSA method. Also, the TGS-ANSA method gave significantly higher results than the chemiluminescence method. At the 200 μg NO_2/m^3 level, the TGS-ANSA, chemiluminescence, and colorimetric methods agreed on the average, but the arsenite method gave significantly higher results. At the 100 μg NO_2/m^3 level, the 3-hour intermittent spike (3B) gave the same results as the 4-hour intermittent spike (3C). However, all the other spiking schedules had different effects on the results with the 9-hour continuous (3D) giving the lowest readings and the 3-hour continuous (3A) giving the highest readings at the 100 μg NO_2/m^3 average level. For the 200 μg NO_2/m^3 concentration, the 22-hour continuous spike (2A) gave results that were significantly lower (α=0.05) than the 6-hour continuous spike (2B).

In a statistical sense, the methods do not give the same results under similar conditions and do not respond to substantial changes in NO_2 levels in the same manner. The length of time NO_2 remains in the air in the absence of possible interfering compounds has a definite effect on daily averages of NO_2 measurements.

Aside from a strictly quantitative analysis of Phase II results, graphical displays of the data are interesting. Figure B-5 illustrates the response of different methods when NO_2 is added into the clean air system at a level of 100 $\mu g/m^3$ on the different spiking schedules. The abcissa of the graph represents the spiking schedule. In general, for the straight 3-hour spike (3B), the values were somewhat closer to the 100 $\mu g/m^3$ horizontal line; and for the 8-hour continuous spike (3D) all values were below the line. The two continuous methods, chemiluminescence and colorimetric, were very close and almost parallel except for the 4-hour intermittent spike (3C). The two manual methods, arsenite and TGS-ANSA, gave parallel responses that were separated in magnitude, with TGS-ANSA always reading lower by approximately 8.6 $\mu g/m^3$. The general pattern of the graphs is probably caused by variations in the addition of NO_2.

PHASE III

Introduction

During Phase III, NO_2 measurements were made using the same NO_2 methods as in Phases I and II. However, in Phase III, three fixed levels of O_3 were combined with two fixed levels of NO_2 in a clean air stream. The purpose of Phase III was to answer the following questions:

1. Do different methods, when used under similar environmental conditions, give the same response within limits of experimental error?
2. Does changing the level of O_3 have any effect on the measurement of NO_2?
3. Does each method respond in the same manner to a change in the O_3 level?

Generalizations beyond those stated above, such as extending the conclusions

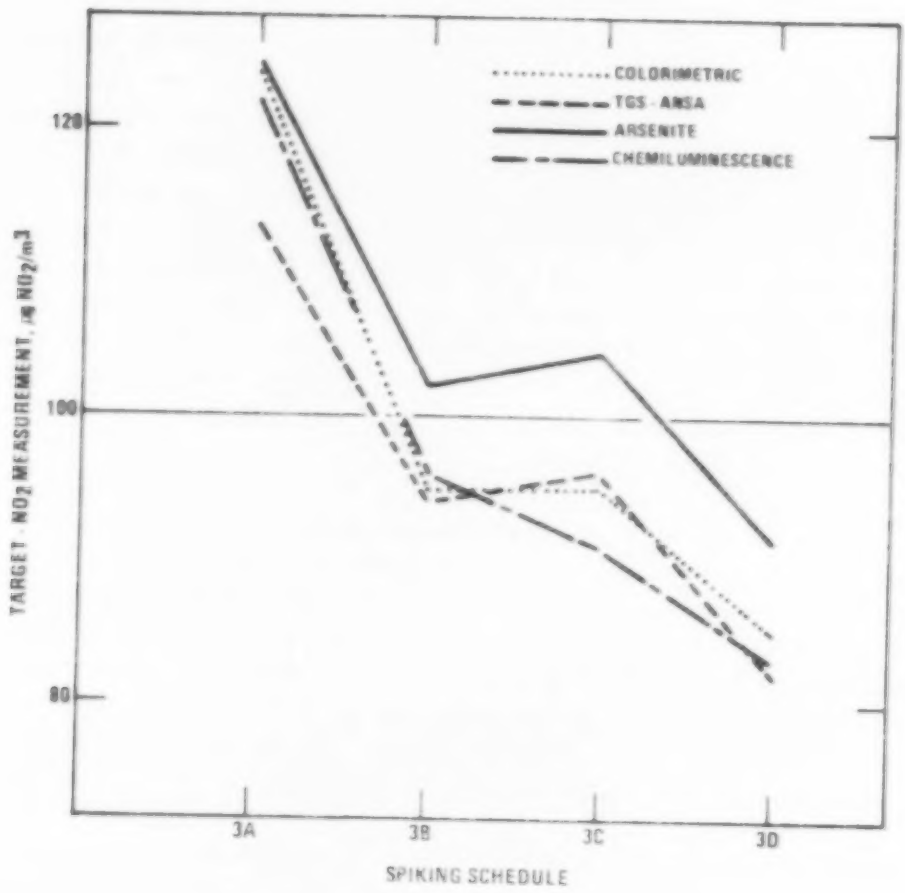

Figure B-5. Phase II - Method difference.

to cover a wider range of NO_2 or O_3 levels, would be misleading. Therefore, we are dealing with a fixed linear model of the form:

$$Y_{ijkl} = \mu + M_i + N_j + O_k + MN_{ij} + MO_{ik} + NO_{jk} + MNO_{ijk} + \varepsilon_{ijkl}$$

where: Y_{ijkl} = The l^{th} observation $l = 1, 2, \ldots n_{ijk}$ on the i^{th} method for the j^{th} NO_2 level and the k^{th} O_3 level: i=1, 2, 3; k = 1, 2, 3

μ = A constant that is common to all observations and is estimated by averaging over observations in the experiment

M_i = The effect of the i^{th} method on the observation. For example, $\mu + M_i$ is the mean of the i^{th} method taken over all mixtures of NO_2 and O_3

N_j = The effect of the j^{th} level of NO_2 on the observation. For example,

$\mu + N_j$ is the mean of the j^{th} level of NO_2 taken over all levels of O_3 and all methods

O_k = The effect of the k^{th} level of O_3 on the observation. For example, $\mu + O_k$ is the mean of the k^{th} level of O_3 taken over all levels of NO_2 and all methods

MN_{ij} = A measurement of non-additivity of the ij cell. For example, the mean of the i^{th} method and j^{th} NO_2 level taken over all O_3 levels may not be $\mu + M_i + N_j$ (additive), but $\mu + M_i + N_j + MN_{ij}$

MO_{ik} = A measurement of non-additivity of ik cell

NO_{jk} = A measurement of non-additivity of jk cell

MNO_{ijk} = A measurement of non-additivity of ijk cell. For example, the mean of the i^{th} method, the j^{th} level of NO_2, and the k^{th} level of O_3 may not be $\mu + M_i + N_j + O_k$ (additive) but $\mu + M_i + N_j + O_k + MNO_{ijk}$

There are i = 4 methods, j = 2 levels of NO_2, k = 3 levels of ozone, and l = observations.

Analysis of Results

To find answers to the questions previously stated, the questions are reformulated in terms of the hypothesis concerning linear combinations to the elements of the linear model and subsequently tested by the appropriate statistical techniques.

An analysis of variance was performed on the data to provide tests of these hypotheses, and the results are summarized in Table B-9.

Each line in the table (excluding error) corresponds to a specific hypothesis. Rejection of a hypothesis, as indicated in the table, means that the probability of making a wrong statement based on the calculated F statistic is a very low 0.01.

The data in Table B-9 indicate that the methods in general give different NO_2 readings, and that O_3 affects the measuring capabilities of the different methods.

To find out which methods gave different readings and also which methods were affected by the presence of O_3, a Duncan's Test procedure was used. This is summarized in Table B-10. Any two means not underscored are significantly (α=0.05) different; whereas, any two means underscored by the same line are not significantly different. Figure B-6 shows how the different methods compare in measuring NO_2 at approximately 75 $\mu g\ NO_2/m^3$ at three different O_3 levels. Figure B-7 is similar graph for comparing methods as to their ability to measure approximately 150 $\mu g/NO_2/m^3$ in the presence of three different concentrations of O_3.

Table B-9. ANALYSIS OF VARIANCE-PHASE III

Source	DF[a]	Sum of Squares	Mean Square	F
Method	3	0.0037885	0.001222	462.17[b]
O_3	2	0.00034285	0.0036737	62.74[b]
NO_2	1	0.2124812	0.1779864	7776.73[b]
Method X O_3	6	0.0018597[illegible]	0.000312165	113.44[b]
Method X NO_2	3	0.00017399	0.00005391	21.22[b]
O_3 X NO_2	2	0.00053495	0.00027840	97.90[b]
Method X O_3 X NO_2	6	0.00022950	0.00003825	14.00[b]
Error	47	0.00012642	0.00000273	
Total (corrected)	70	0.02[illegible]		

[a] DF = degrees of freedom.
[b] Hypothesis rejected at the 0.01 level.

Table B-10. DUNCAN'S TEST-PHASE III

Methods[a]:	COLOR	CM	TGS	ARS
Means	73.1	98.3	110.2	110.4

Ozone:	353	667	100
Means	98.5	99.6	107.9

Method X ozone:

C-667	C-353	CM-353	CM-667	CM-100	CL-100	TGS-353	AS-353	TGS-100	AS-667	AS-100	TGS-667
43.2	71.8	92.5	100.6	101.9	104.3	106.6	106.6	107.5	111.9	112.8	117.1

[a] Colorimetric (COLOR), chemiluminescence (CM), TGS-ANSA (TGS), arsenite (ARS).

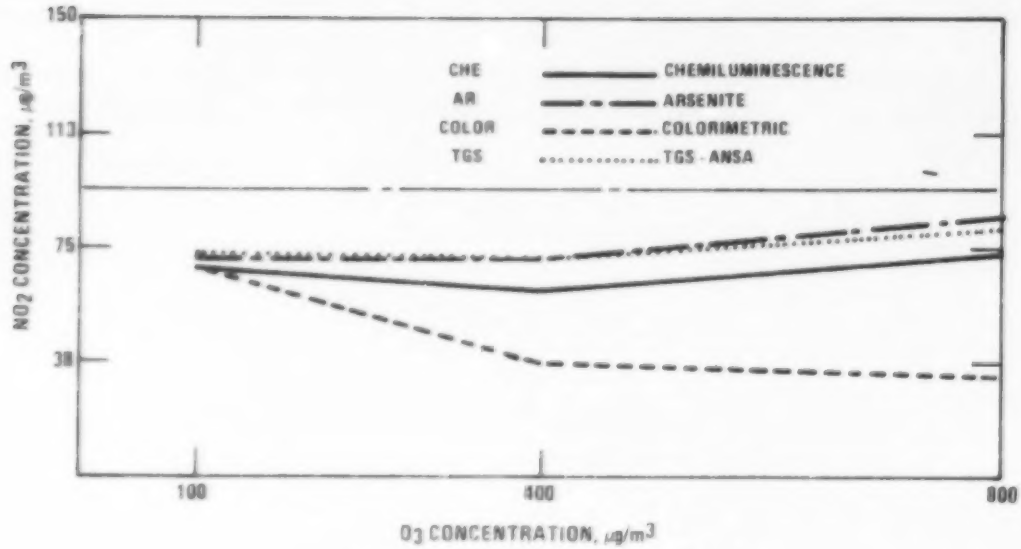

Figure B-6. Ozone interference - 75 $\mu g/m^3$.

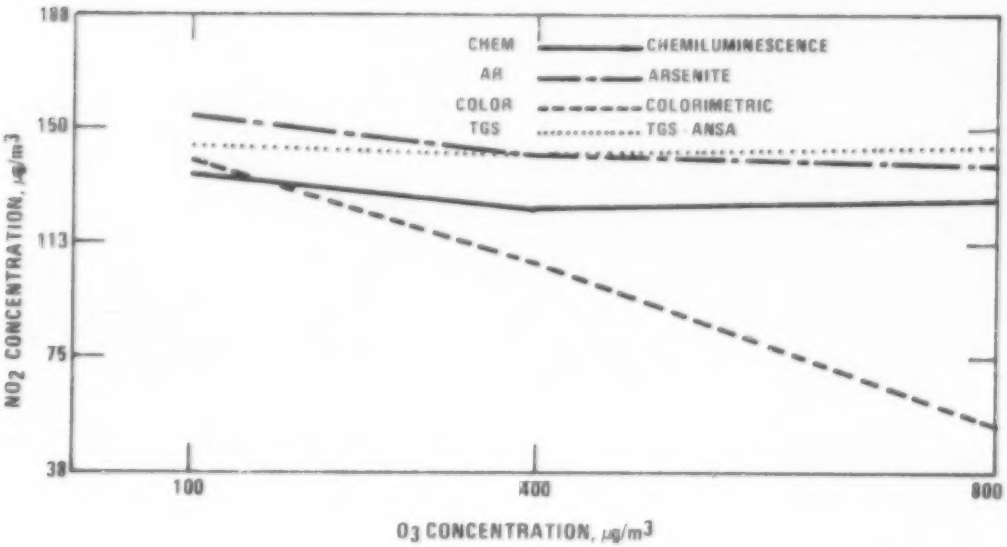

Figure B-7. Ozone interference - 150 $\mu g/m^3$.

Conclusions

The results of Duncan's Test indicate that, on the average, the arsenite and the TGS-ANSA methods gave the same NO_2 values but that the chemiluminescence method values were slightly lower. However, the colorimetric method was subject to the greatest interference; it gave significantly lower readings at both the 353 and 667 $\mu g/m^3$ levels. Also, the colorimetric method readings were significantly lower at the 667 $\mu g/m^3$ level than at the 353 $\mu g/m^3$ level. The chemiluminescence, arsenite, and TGS-ANSA methods did not seem to be affected by changes in the O_3 level.